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## Manchester Section.

Meeting held at Grand Hotel, on Friday, March 3rd, 1916.

MR. J. H. HOSEASON IN THE CHAIR.

### A NOTE ON THE CHROMIUM INTENSIFICATION PROCESS.

BY R. E. CROWTHER.

The so-called "Chromium" process of intensification of silver photographic images came into prominence in 1905 when Welborne Piper and D. J. Carnegie published important details arrived at by the modification of the original formula of Eder (1881).

The process comprises two operations (exclusive of washings), viz., "Bleaching" and re-developing, and according to the constitution and time of action of the "bleaching" bath, more or less intensification may be obtained.

The following formulæ were recommended:—

	A.	B.	C.	Eder's.
Potassium bichromate ...	1 grm.	2 grms.	2 grms.	2 grms.
Hydrochloric acid (1·16 sp. gr.) .....	0·2 c.c.	1·0 c.c.	4·0 c.c.	6·0 c.c.
Water to .....	100 c.c.	100 c.c.	100 c.c.	100 c.c.

Bleaching with bath A yields the greatest intensification, baths B and C yield progressively less, whilst the use of Eder's bath effects very little increase of density of the image. The working details of the process and the copious notes of the two authors above referred to leave little to be desired as far as the application of the process is concerned, but the chemical reactions which lead to the excellent and permanent results were not elucidated.

The difficulties encountered when attempting quantitative work with small amounts of silver were augmented by the presence of various compounds which appear to be constituents of all developed and fixed photographic images. Attempts were made to obtain quantitative results by the use of silver wire, but the action of the "bleaching" baths on the metal in this condition was inordinately slow and the quantitative work was therefore abandoned.

Piper has subsequently (private communication) expressed the opinion that the chromium in the "bleached" silver-chromium complex is in the chromous condition, but the existence of a chromous compound which exhibits reduction reactivity of a degree sufficient to decompose water (see "Reduction methods of volumetric analysis," Knecht and Hibbert, p. 104) in the presence of an energetic oxidiser such as potassium bichromate, appeared to be highly improbable, and the present author therefore endeavoured to determine the state of oxidation of the chromium in the complex.

A carefully prepared silver mirror was used as the "image" and the chromium present in the "bleaching" baths and in the "bleached" image was determined by means of a solution of titanous chloride. The influence of the hydrochloric acid on the bichromate was eliminated by working against a "blank." The mirror showed a metallic silver content of 99·83% (mean of two determinations).

It will be evident that if the silver reduces the chromium to the chromous state only half the weight of bichromate will be reduced as compared with that which would be reduced were the reaction to terminate when the chromic condition had been attained.

Using Eder's formula on 0·3190 grm. Ag it was found that 108 Ag = (a) 7·95 and (b) 8·0124 grms. O from bichromate, and that the whole of the reduced chromium passed into solution in the bleaching bath.

Using the formula B above on 0·1316 grm. Ag. the result 108 Ag = 7·9796 grms. O from bichromate was obtained. In this case a proportion of the reduced chromium compound was attached to the silver chloride. After treating the "bleached" mirror with dilute sulphuric acid it was completely soluble in ammonia solution and the acid liquor contained exactly the amount of chromium which the bleaching bath lacked in order to give the result indicated.

Thus intensification was due to a precipitate of a chromic compound. The conditions, when bath A is used for bleaching, are not quite so simple as in either of the two cases cited above. The amount of CrO<sub>3</sub>, apparently reduced is always in slight excess of that which would agree with theory. The excess was found to be represented by unreduced CrO<sub>3</sub>, which is combined with the precipitate, to which it imparts a brown colour and from which it cannot readily be separated without the use of acid washings.

The brown precipitate appears to be similar to that which is formed when a solution of potassium bichromate is reduced at the boil with an amount of sodium sulphite insufficient to reduce that part of the chromium which forms the bi-chromate, i.e. the CrO<sub>3</sub> in K<sub>2</sub>CrO<sub>4</sub>.CrO<sub>3</sub>.

The colloidal nature of the chromic hydroxide precipitated under these conditions, the relatively small amount of CrO<sub>3</sub>, which is attached to it, and the fact that this amount was governed by the final CrO<sub>3</sub> content of the reacting solutions, point to the conclusion that the brown precipitate is an adsorption compound of either CrO<sub>3</sub> or the bichromate and basic chromic hydroxide.

It has been shown that the brown complex of a "bleached" negative whilst being readily attacked by dilute mineral acids is relatively highly resistant towards a 2% aqueous solution of potassium metabisulphite. In this respect it is quite analogous to the brown precipitate formed by the action of sulphite on bichromate. Further the analogy extends to the action of alkaline photographic developers which reduce the CrO<sub>3</sub> in each complex with a resulting change in the colour of the complex from brown or buff to olive green. Eder's solution in conjunction with titanous chloride titration may be used for the estimation of the metallic silver content of photographic images (developed).

### THE PREVENTION OF REVERSAL OR SOLARISATION IN PHOTOGRAPHIC NEGATIVES.

BY R. E. CROWTHER.

Of the various conditions which lead to the formation of a reversed result when an exposed photographic emulsion is developed in the ordinary way, this communication deals only with those which may be conveniently grouped under the term "Over Exposure."

Such over exposure may be constituted by abnormally prolonged action of a light of average

intensity or by relatively shorter exposure to a highly actinic light.

The former condition is frequently encountered in the photographing of interiors when the subject includes unscreened windows at one end of the actinic scale and heavy shadows at the other end of the scale; the latter condition may be met with in the photographic investigation of various light sources such as the sun, the electric arc, etc. Jannsen (*Comptes rend.*, 90, 1447; 91, 119) observed, when photographing the sun, that as the exposures were prolonged the developed results were positives where they should have been negatives, and also that still longer exposures yielded negative developed results again.

These phenomena of reversal and re-reversal have excited considerable interest amongst photographic experimenters, their cause has been the subject of much speculation, and means for their prevention have been sought by many investigators with varying degrees of success.

The so-called gelatin dry plate process originated in 1871 in some experiments of R. L. Maddox, who prepared a gelatin emulsion which, whilst being very imperfect, was nevertheless workable. Maddox's emulsion contained an excess of silver nitrate and was developed with a plain solution of pyrogallol. In 1873 it was pointed out that removal of the excess silver nitrate and of the soluble reaction products led to improved results, i.e., in the presence of gelatin any other halogen accommodator was not necessary, and that bulk washing of the prepared emulsion could advantageously replace the tedious process of dialysis. The advantage of precipitating the sensitive compounds in the presence of a little gelatin was also first commented on in this year.

In 1878 Chas. Bennett discovered the increase in "speed" which resulted from the preparation of the emulsion at the temperature of boiling water, at which temperature it should be maintained for some time before washing out the soluble reaction products. The use of a little ammonia in addition to heating, or even without heating, the emulsion for the production of greater speed, is perhaps the only published modification of Bennett's process which is of interest, and, although the details of the manufacturing processes of the modern dry plate are well guarded trade secrets, it may be taken for granted that, as far as essential ingredients are concerned, Bennett's formula is typical. The gelatin in the emulsion of the modern dry plate therefore acts both as the emulsifier and the sensitiser. Whilst its properties as an emulsifier leave little to be desired, as a sensitiser it is far from ideal.

The ideal sensitiser would exhibit the following properties:—Absolute stability under temperate, tropical, or frigid atmospheric conditions; power to accommodate the halogens instantaneously, yielding stable compounds having no action on emulsion, developer, or image. Solubility in water and alcohol and a colloidal structure are also desirable characteristics. Such a sensitiser has yet to be discovered.

Various substances are at present employed as sensitisers, e.g., a soluble silver salt is used in printing-out emulsions, its action being to accommodate the halogen liberated by light action by converting it into insoluble silver halide. This is again decomposed by light action, whereupon the accommodation again takes place, and so on, until sufficient silver is produced per unit area to yield a visible image.

Since in the case of negative emulsions the exposures usually given are very much less than that required to yield a printed-out image, it might be concluded that for this class of emulsion

the presence of a sensitiser is not necessary. As far as normal exposures are concerned there is no need whatever for a sensitiser provided the halogen be allowed to get away from the silver, as the experiments of Daguerre, Herschel, and more recently those of Dr. H. Welsz (*Brit. J. Phot.*, 1907, p. 960) prove.

There is distinct evidence, however, that long before a visible image has been produced by the action of light on a gelatino-bromide emulsion bromine is liberated and its presence in the emulsion, as would be anticipated from theoretical considerations, retards the further decomposition of silver bromide. Thus a sensitiser confers printing-out speed on an emulsion. It does not necessarily affect the speed of an emulsion in the Hurter and Driffield sense. The H. and D. "speed" of an emulsion is quite distinct from, and probably bears no relation to, the printing-out speed. The H. and D. "speed" is always determined from the results obtained by *exposure and development*, and a moment's consideration will lead to the conclusion that development cannot legitimately be considered as equivalent to a continuation of exposure. In the first place development takes place under conditions (absence of actinic light) which should favour the reverse reactions of those instigated by exposure. Further, the reactions consequent on exposure may be considered as occurring in solid solution and only those portions of the emulsion components which are within molecular distances of each other can react. In a normally dry emulsion there can be little if any migration of silver atoms and the migration of gaseous halogen molecules must be comparatively slow. The conditions may be characterised as unidirectional, there being no evidence of reverse reactions.

In development, solution ionisation and ionic mobility are normal and reactions direct and reverse can proceed in a normal way. Thus, if a gelatino-bromide emulsion be exposed to actinic light in a series of strips for successively increasing periods of time, deposits of silver of successively increasing density are produced up to the limit of the silver contained in the emulsion.

On the other hand, if the deposits be obtained by the combined actions of exposure and development the ultimate densities of such deposits are governed by the concentration, composition, and time of action of the developer.

If the results obtained by exposure and development be represented graphically as a curve the abscissæ of which are log exposures and the ordinates H. and D. "densities" (i.e., weights of silver), we obtain the well known curve which comprises three distinct branches, viz.: (1) a first ascending portion—the normal or first negative portion; (2) a descending portion—the reversal portion; and (3) a second ascending portion—the second negative portion.

It has been stated that Jannsen (*Comptes rend.*, 90, 1447; 91, 119) obtained evidence of repetitions of these portions, but although I have given exposures ranging up to 300 hours summer sunshine to a Kodak film emulsion no evidence of any such repetition was obtained on development (see also H. J. L. Rawlins; this *Journal*, 1891, p. 18). Failing further evidence, therefore, it may be assumed that the second negative portion is the last portion of the curve.

Using a film of pure silver bromide, i.e., free from a sensitiser, there is reason to believe that both the latter portions of the curve, i.e., the reversal and second negative portions, are absent. My experiments with a film of pure silver bromide are not sufficiently advanced to be presented as conclusive evidence, but as far as they have gone

they confirm the results obtained by H. Weisz, who found that with such a film exposures long enough to produce a distinct printed out image yielded no reversal phenomena on development. As has been previously pointed out, exposures of very much shorter duration than are necessary to obtain a printed out image give distinctly reversed results on development where a gelatino-bromide film is employed.

These facts possess more than a passing interest to a student of the latent image in a gelatino-bromide emulsion. Hitherto, most of the work which has been done on this question has been concerned solely with the metallic element, to the neglect of any consideration of the influence of the non-metallic component (see however Trivelli, *Phot. Korr.*, 1911, 24, 182, and Lippocramer, *Z. Chem. Ind. Koll.*, 1911, 9, 22–25; also Lumière and Seyewetz, *Bull. Soc. Chim.*, 1908, 3, 743–750).

The evidence of the later workers seems to support the assumption that the latent image consists of colloidal silver in solid solution in unaltered silver bromide and of loosely combined halogen rather than of silver sub-bromide,  $\text{Ag}_2\text{Br}$  (K. Sicking, this J., 1911, 833, and Reinders, this J., 1911, 446, 027, 1231).

According to this conception the exposure of a gelatino-bromide emulsion to actinic light causes a severance of the bond between the silver and the bromine. Both these components are in an ionised state and hence are chemically active.

The bromine attaches itself to the gelatin in some such way as indicated by H. R. Procter (*Chem. Soc. Trans.*, 1914, 313). According to this worker gelatin forms an addition compound of an ammonium type with the halogen acids. In this case the halogen acid results from the interaction of the bromine on the small amount of water present in a normal emulsion (a perfectly desiccated emulsion is insensitive). Nascent oxygen is also thus produced and this accounts for the tanning action which can be observed in an exposed emulsion. It appears probable that the tanning is effected by dehydrogenation and subsequent quinone condensation of the dehydrogenated products.

The severance of the bond uniting the metal and the halogen necessitates the application of a definite minimum amount of energy; exposures representing less than this minimum may cause a straining of the bond, but on the termination of the exposure normal, i.e., unaltered, molecules remain. In one branch at least of applied photography this inertia of the emulsion has to be considered; thus in stellar photography it has been found that telescopes having object glasses of relatively small diameter are incapable of producing developable images of the fainter stars, no matter how long the exposure, whereas a larger diameter objective produces developable images.

Adopting the nomenclature of E. C. C. Baly, it may be stated that the action of the light opens closed force fields of the silver-halogen molecule, and in order to produce a developable condition the respective atomic fields must be so far separated as to allow of their stabilisation by interaction with suitable contiguous substances. The capacity to resist this action of the light is a measure of the true inertia of the sensitive compound which should not be confused with the apparent inertia as determined by the Hurter and Driffield system. This latter is determined from results obtained by the combined actions of exposure and development and for a given exposure can be modified by alteration of the development conditions or of the physical condition of the emulsion.

Thus, Sheppard and Mees have shown that, other things being constant, certain developing agents lower the H. and D. inertia of an emulsion and it is further well known that using the same constituents in their manufacture a "ripened" emulsion exhibits a lower H. and D. inertia than an "unripened" emulsion.

Kinoshita (*Proc. Royal Soc.*, 1910, A 83, 432), has shown that if one molecule of silver bromide in any aggregate of molecules, or grain, is ionised, the whole grain becomes developable and therefore the mere aggregation of molecules which occurs in the ripening process is sufficient to account for the increase in the "speed" when such "speed" is determined from the relationships of the visible developed deposits.

It might at first sight appear that the presence of a reducing agent in the emulsion should, by the more rapid removal of the halogen liberated or ionised by exposure, decrease the inertia, but in this connection it is necessary, bearing Kinoshita's results in mind, to remember that the light energy necessary to produce a developable condition is exceedingly small in amount. Thus, according to the calculations of Nutting the amount of light energy applied to an emulsion which on development will yield unit density (arresting  $\frac{1}{100}$  of the incident light) is of the order of  $10^{-14}$  ergs per grain of  $\frac{3}{4}$  diameter or  $10^{-7}$  ergs per sq. cm. of the emulsion. Provided therefore the halogen from one molecule per grain (of  $10^{11}$  molecules) can be accommodated the full "speed" of the emulsion may be obtained. The presence or absence of an energetic reducing agent in the emulsion can make no appreciable difference to the speed of that emulsion.

I have endeavoured to show elsewhere (*Phot. J.*, 1914, 250 *et seq.*, and 1915, 186 *et seq.*) that, as exposure is increased and the amount of halogen liberated is also increased, the presence of an active reducing agent in the emulsion modifies its properties appreciably. When the gelatin itself acts as the reducing agent by virtue of its power of combining with halogen acids, as before pointed out, it is quite efficient for all ordinary purposes.

With increased exposure the further liberated halogen is mechanically held by the gelatin until such exposures as are sufficient to cause the expulsion of gaseous halogen from the film are employed. The development reactions under these varying exposure conditions can be the more readily described if we assume that a gelatino-bromide emulsion has been exposed in three strips; the first strip having received an exposure which develops to a density of unity, the second strip, such as develops to a reversed result, and the third strip, an exposure which yields the so-called second negative.

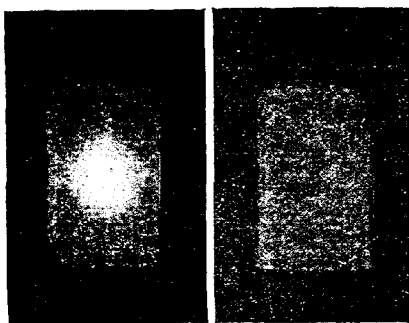
The development of strip (1) results from the electrolytic reduction of each grain in which ionisation has occurred during exposure, the developed density accruing from the reduction of those molecules of silver bromide which were not affected by light.

In the case of strip (2) a small amount of silver—produced by the exposure—generally just discernible as a printed out image—is augmented by a small amount produced by a reaction similar to that occurring in the case of strip (1), but the concentrations of the oxidation products of the development base, and of the alkali halide increases so rapidly by the action of the occluded halogen in the gelatin that rehalogenisation of both deposits commences immediately and rapidly proceeds to a finish, when development is performed in non-actinic light.

This initial development and subsequent disappearance can be readily observed with suitably exposed emulsions when well diluted developers are employed. If development be conducted in actinic light the rehalogenisation is never complete, in fact it has been shown that a developed reversed image may be redeveloped to yield a normal result after exposure to actinic light.

The reactions which cause the rehalogenisation are in all probability exceedingly complex, but that the oxidised products of the developer are the cause seems certain. If, for instance, a small quantity of quinone is placed on a normally exposed emulsion and the image then carefully developed, complete reversal will occur in the areas which were in contact with the quinone.

In this connection it is of interest to recall the fact that Lumière and Seyewetz have made use of the combined action of an oxidised developing base and an alkali halide for the reduction of developed images (this J., 1910, 1228). The somewhat remarkable oxidising power (by dehydrogenation) of bodies of a quinone structure has been commented upon by A. G. Green (J. Soc. Dyers and Col., 1913, 109).



Strip (3). In this case the final developed deposit consists of the silver formed during exposure *minus* that rehalogenised by reactions similar to those occurring in strip (2). Obviously, the longer the exposure the denser will the developed result be, because once the film has taken up its full complement of halogen the remainder of the halogen passes into the atmosphere and is no longer available for the oxidation of the developer and hence for the rehalogenisation of the silver.

The prevention of reversal is therefore dependent upon the effective accommodation\* of the halogen, liberated during exposure, in such a way that the developer employed cannot be oxidised by the reaction products of such accommodation. Various substances have been added to the emulsion for this purpose and as far as efficiency is concerned potassium nitrite, as recommended by Abney, is perhaps the most important, but its tendency to crystallise and cause reticulation of the film prevents its use in the case of the gelatino-bromide dry plate.

Other more or less readily oxidised compounds, e.g., manganous salts, quinone, and *m*-phenylenediamine have been tried, but although they undoubtedly improve the results they do not react

with the halogen quickly enough to prevent a large proportion of it from reacting with or otherwise being accommodated by, the gelatin: this, of course, largely annuls the beneficial effects of the special additions.

The bases used for development are amongst the most active reducing agents which can be used for the accommodation of the halogens and they can be used as sensitisers in a gelatino-bromide or chloride emulsion. With one or two exceptions, however, these developers cannot be employed in emulsions which have to be developed, as their oxidation products, formed during exposure, are, in conjunction with the alkali bromide, exceedingly active rehalogenisers. (The actual composition of the rehalogenised compound is at present unknown—it is completely soluble in a 10% solution of sodium thiosulphate.)

Broadly speaking, the slower a developer acts in the normal way the less is the apparent reversing power of its oxidation products and hence these slow developers are applicable as sensitisers which greatly minimise solarisation phenomena. Compounds of hydrazine and hydroxylamine have been successfully used in this connection (Eng. Pat. 1889 of 1908) but a serious diminution of the "speed" appears to result from their addition to rapid emulsions.

Highly beneficial effects are produced by the addition of one or other of the compounds derived from *p*-phenylenediamine for the use of which, as preventatives of reversal, a patent has been taken out by the author (Eng. Pat. 29,919 of 1912). *p*-Phenylenediamine itself may be employed but the rapidity with which it is oxidised by air forming highly coloured bodies which "slow" the emulsion renders it highly desirable to protect the amino groups. When these groups are so protected the "slowing" of an emulsion by the addition of one or other of the compounds specified in the patent is for all practical purposes quite negligible.

It is necessary, when using plates which have been rendered more or less immune from reversal faults, to develop with care if negatives showing detail in both high lights and shadows are desired. The reasons for this have been discussed more fully in a short communication to the Royal Astronomical Society (J. Roy. Astron. Soc., 1914, 24, [5], 261). In fine, the golden rule of "Expose for the shadows and develop for the high lights" with one or other of the "soft" working developers, should be followed. Ordinary dry plates may be either steeped in the diamine solution or the latter may be applied with a "Blanchard" or camel hair brush, and as alteration in the air is exceedingly slow the plates so treated may be stored under normal conditions until required for use. The two examples accompanying this communication—photographs of an eleven ampere arc—were obtained by exposing in a stereoscopic camera, an ultra rapid plate half of which had been treated (some days previously) with a 1% solution of a substituted *paraphenylenediamine*. The exposure given was 11 seconds at an aperture of *F*/8 and development was performed on the uncut plate so that both halves were developed in identically the same way. In this particular instance a developer containing *p*-phenylenediamine hydrochloride and sodium sulphite only was employed, as it had been previously noticed that such a solution yielded excellently graded negatives of subjects showing enormous contrasts. The examples are from "straight" prints from the unretouched negative and show that the *p*-phenylenediamine compounds can be usefully employed for the purpose of minimising the reversal effects of over-exposure.

\* It is remarkable that direct halogen absorbents will neither revert reversal nor serve as developers.

## Journal and Patent Literature.

PATENT SPECIFICATIONS may be obtained by post by remitting as follows:—

*English*.—6d. each, to the Comptroller of the Patent Office, Southampton Buildings, Chancery Lane, London, W.C.  
*United States*.—1s. each, to the Secretary of the Society, who has to furnish the U.S. Patent Office with the following data:—Patent number, date, name of patentee, and title of invention.  
*French*.—1 fr. 05 c. each, as follows: Patents dated 1902 to 1907 inclusive, Belin et Cie., 56 Rue Feron 8, Paris (3e); Patents from 1908 to date, L'Imprimerie Nationale, 87, Rue Vieille du Temple, Paris.

### I.—GENERAL; PLANT; MACHINERY.

#### PATENTS.

*Furnaces and kilns for applying and utilising heat of combustion.* G. Six, and O. Guttman and Sons, London. Eng. Pat. 4226, Mar. 17, 1915.

A HORIZONTAL muffle furnace is provided with an agitator, the rake fingers of which are splayed at their lower ends and bent in the direction of the exit of the furnace. The rakes are moved reciprocally with respect to the furnace by means of rods or tubes or an endless chain and a motor. The bed of the furnace consists of cast iron plates arranged step fashion. The arrangement is applicable to furnaces for the manufacture of sodium sulphate and hydrochloric acid.—W. H. C.

*Liquid fuel furnaces.* H. E. Yarrow, Glasgow. Eng. Pat. 17,450, Dec. 13, 1915.

IN a boiler furnace burning oil fuel, the lever which controls the oil supply is connected by links to the air doors of the corresponding air-box so that the doors are opened and closed simultaneously with the opening and closing of the oil-supply valve. The mechanism may be locked in the open and closed positions.—W. F. F.

*Regenerative-furnace.* J. W. Barnes, Youngstown, Ohio. U.S. Pat. 1,186,370, June 6, 1916. Date of appl., June 17, 1915.

THE furnace is provided at each end with a gas nozzle projecting into the hearth chamber and with air and gas regenerating chambers. Valves are provided for changing the direction of the flow of the air and the gas.—W. H. C.

*Gas burner; Industrial — and furnace wherein the same can be used.* South Metropolitan Gas Co., and D. Chandler, London. Eng. Pat. 100,603, Jan. 15, 1916. (Appl. No. 685 of 1916.)

THE injector tube of the burner is mounted on an annular plate and projects into the furnace, while the gas-supply pipe and nozzle are pivoted on a lug projecting outwards from the annular plate, so that the supply pipe is parallel to the plate and the nozzle at right angles. The supply pipe is normally fixed at another point to another lug projecting from the annular plate, by a cotter pin which can be withdrawn, so that the tube may swing outwards to facilitate cleaning of the injector tube. The furnace contains a layer of refractory material below the crucible and slightly below the burner flames.—W. F. F.

*Furnace.* W. P. Brown, London, Ontario. U.S. Pat. 1,184,819, May 30, 1916. Date of appl., Apr. 12, 1915.

THE furnace is provided with a grate, smoke outlet, fire-box, and a gas-collecting and separating chamber, located within the furnace at a point higher than the smoke outlet, and out of and above the direct line of draught from the fire-box to the smoke opening. The lighter gases of combustion rise into the gas-collecting chamber, and separate into gases of different densities. The lightest gas is conducted back to the fire-box by a return flue from the chamber, terminating in and encircled by an air inlet flue on the side of the fire-box above the grate, and provided with openings communicating with the fire-box.—B. N.

*Gas and liquid coolers and gas scrubbers.* W. Yates, and Matthews and Yates Ltd., Manchester. Eng. Pat. 8762, June 14, 1915.

A NUMBER of thin discs are threaded closely together on a rotating horizontal shaft in a casing containing water up to the level of the shaft. Air or gas enters the casing by an opening opposite the edges of the discs and passes between them to a similar outlet at the opposite side. Short-circuiting over the top of the discs is prevented by horizontal guide-plates which extend from the side of the casing to the edges of the discs.

—W. F. F.

*Dust or like matter from air or gases; Apparatus for separating — and collecting same.* G. Dod, Prestwich, and The Imperia Co., Ltd., Manchester. Eng. Pat. 8920, June 17, 1915.

THE dust-laden air is delivered downwards into a removable collecting chamber, which is pressed against a stationary upper chamber and is provided with a lever operated by hand for disengaging it from the upper chamber.—W. H. C.

*Steam boilers; Preventing incrustation in —.* R. Seabrook, Grimsby. Eng. Pat. 10,930, July 28, 1915.

BRIMSTONE (sulphur) is added to the water to prevent incrustation.—W. H. C.

*Boiler-cleaning composition.* G. W. Wallace, East St. Louis, Ill., Assignor to Halene Products Co., St. Louis, Mo. U.S. Pat. 1,182,947, May 16, 1916. Date of appl., July 19, 1915.

THE composition consists of a solution of naphthalene in a hydrocarbon oil of the "benzin series" having a low specific gravity.—W. H. C.

*Mixing apparatus; Chemical —.* J. Dean and B. N. Dodge, Bradford. Eng. Pat. 13,044, Sept. 13, 1915.

A MIXING apparatus for chemicals is provided with heating or cooling coils made in the form of jointless U-shaped pipes which depend from the cover of the vessel and are provided with a siphon pipe for the extraction of the condensed water.

—W. H. C.

*Mixing and kneading machines.* J. Lips, Nieder-Urdorf, Switzerland. Eng. Pat. 100,611, Feb. 23, 1916. (Appl. No. 2733 of 1916.)

A MIXING and kneading machine has two kneading implements rotatable on crank pins and provided with arms placed crosswise and connected by links with a fixed stud, which takes the stresses due to the resistance of the material being kneaded. The rotating kneading pan is removable and is mounted on a carriage provided with studs, so that it can only be rotated when it is in its proper position in relation to the kneading arms.

—W. H. C.

*Evaporating apparatus.* W. Anderson, Helensburgh, and J. Meikle, Glasgow. Eng. Pat. 15,547, Nov. 4, 1915.

THE first unit of a multiple-effect evaporator consists of upper and lower liquid-containing drums connected by vertical pipes, which pass through a flue wherein they are heated by the

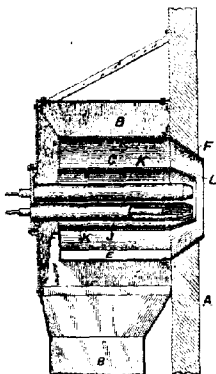
fire gases. A vapour- and liquor-containing drum is fixed above the upper liquid-containing drum and is connected therewith by pipes. The uppermost drum is also provided with a feed inlet pipe and a pipe which passes through the upper liquid-containing drum and the flue into the lower liquid-containing drum.—W. H. C.

*Concentrating aqueous liquids; Process of*—E. Collett. Assignor to Norsk Hydro-Elektrisk Kvaestofaktieskab, Christiania, Norway. U.S. Pat. 1,184,926, May 30, 1916. Date of appl., Nov. 25, 1913.

THE liquid is evaporated by indirect heating and the vapours given off are conducted into the lower part of a drying apparatus charged with a drying agent. The middle portion of the drying apparatus is maintained at a temperature suitable for the drying process by withdrawing a portion of the liquid flowing through the apparatus, cooling it, and reintroducing it into the apparatus at a higher point. The drying agent after passing through the apparatus is introduced into the liquid being evaporated, to recover any vapour other than water vapour which may have been absorbed.—W. H. C.

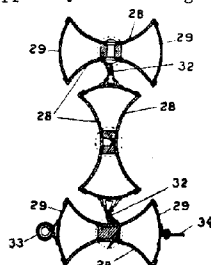
*Desiccating apparatus.* O. E. and I. S. Merrell, Assignors to Merrell-Soule Co., Syracuse, N.Y. U.S. Pat. 1,183,098, May 16, 1916. Date of appl., Apr. 4, 1910.

AN air whirling chamber, C, having tangential inlets, E, from the wind trunk, B, by which it is surrounded, communicates with a desiccating chamber, A, by a conical opening, F. It is also provided with a central air pipe, K, also having a conical orifice, L, the cone being more acute than the cone, F. The liquid to be desiccated is sprayed into the chamber by a number of atomisers, J.—W. H. C.



*Drying apparatus.* H. C. Ebel, Hanover, Germany. U.S. Pat. 1,176,706, Mar. 21, 1916. Date of appl., Aug. 10, 1915.

A TALL, narrow, vertical drying chamber is provided with a series of superposed conveyors, each consisting of a pair of oppositely curved troughs, 28, connected by convex longitudinal plates, 29, and circular end plates, and mounted on a rotating shaft. Scrapers, 32, 33, or 34, attached to the longitudinal plates, sweep over the surface of the troughs. Adjacent conveyors revolve in opposite directions, and the material, supplied to the uppermost one, falls into the next lower one, and so on, to a screw conveyor at the bottom. Air, heated in suitable heating chambers on either side of the drying chamber, is passed through the latter.—W. H. C.



*Cooling or heating liquids or gases or treating air or gases with liquids; Apparatus for*—G. H. Walker, Malvern, and H. Heenan, Manchester. Eng. Pat. 8676, June 12, 1915.

IN cooling or heating apparatus consisting of two or more rotary drums formed of a number of convolutions of sheet metal, and mounted on a vertical shaft, so arranged that the gas passes vertically between the convolutions, guide-plates are provided between each pair of drums to collect the drops of liquid from the upper drum, and deliver the liquid as a constant stream to the drum below. A fan or propeller is also provided to create a draught.—W. H. C.

*Liquid-cooling tower.* G. J. Stocker, St. Louis, Mo. U.S. Pat. 1,187,399, June 13, 1916. Date of appl., Mar. 26, 1914.

THE liquid to be cooled trickles down against a current of air, over a cooling surface composed of layers of parallel, spaced, horizontal slats set up on edge, the slats in each layer being at right angles to those in the adjacent layers. Diagonal vertical slats pass down through the passages thus formed, to bind the structure.—W. F. F.

*Raising or forcing liquids or elastic fluids; Apparatus for*—H. A. Humphrey, London, and W. J. Rusdell, Wolverhampton. Eng. Pat. 8890, June 16, 1915.

IN internal combustion pumps described in Eng. Pat. 11,818 of 1911 (this J., 1912, 626), energy is stored by compression only when the power stroke exceeds the normal stroke in length. The external work is done on the power stroke and the compression of the fresh combustible charge on the following stroke. The lengths of the strokes are maintained within the desired limits by causing the pressure changes in the elastic cushion or cushions to control the supply of combustible mixture. The motion of the reciprocating part of the pump is transformed into rotary motion for the purpose of operating the inlet and exhaust valves.—W. H. C.

*Freezing water-bearing strata in boring operations and the like; Process for*—A. Notzny, Gleiwitz, Germany. Eng. Pat. 16,825, Nov. 30, 1915.

LIQUEFIED air is injected into the strata or into pipes lining the borehole and by its evaporation effects the freezing.—W. H. C.

*Tube-mill.* D. E. Carlson, Assignor to Chalmers and Williams, Inc., Chicago Heights, Ill. U.S. Pat. 1,183,431, May 16, 1916. Date of appl., July 14, 1915.

A DIAPHRAGM for a tube-mill is formed of two plates adjustably secured together and having overlapping perforations. Projections from one of the plates extend into the perforations of the other plates.—W. H. C.

*Pulverising-mill.* M. R. O'Shaughnessy, Elmsdale, Nova Scotia. U.S. Pat. 1,185,342, May 30, 1916. Date of appl., July 28, 1915.

A REVOLVING tube mill is divided into compartments by transverse partitions provided with radial convolutions, which increase in depth outwardly. The mill has an axial inlet at one end, an axial outlet at the other, and axial communicating openings in the partitions. The size of the openings increases from the inlet to the outlet.—W. H. C.

*Grinding-mill or crusher.* C. Goldammer, Kattowitz, Germany. U.S. Pat. 1,186,476, June 6, 1916. Date of appl., July 31, 1915.

AN upper grinding roller is mounted horizontally in fixed bearings in two parallel frames, and by its

rotation drives a grinding ring surrounding and supported by it. Two other grinding rollers are mounted in bearings carried by levers pivoted to the side frames and rest in the lower part of the grinding ring. A surrounding casing is removable in sections without affecting the adjustment of the rollers.—W. F. F.

*Bone-black or other filtering media; Process of and apparatus for revivifying or decarbonising*—. M. Weinrich, New York. U.S. Pats. 1,184,397 and 1,184,398, May 25, 1916. Dates of appl., Nov. 19, and Dec. 13, 1915.

THE material is heated in a closed chamber by external means and is then discharged from the perforated bottom of the chamber in fine streams into another chamber where it comes into contact with a current of air; or it may be passed through a revolving drum heated externally by fire gases and provided inside with perforated lifting blades through which the material is discharged in thin streams against a current of air passing through the drum.—W. H. C.

*Colloidal solutions in organic substances not miscible with water; Process of producing*—. H. Karplus, Berlin. Eng. Pat. 8641, June 11, 1915.

AN irreversible colloid is removed from a hydrosol by producing within the latter an amorphous organic precipitate which is soluble in the organic substance in which it is desired to produce the organosol. The precipitate is separated, heated to remove water, and then mixed with the organic substance, when an organosol of the desired colloid is obtained. Organosols suitable for use as pharmaceutical products, lubricants, catalysts, pigments, etc., may be prepared in this way. (Reference is directed, in pursuance of Sect. 7, Sub-sect. 4, of the Patents and Designs Act, 1907, to Eng. Pat. 2382 of 1891; this J., 1892, 360.) —W. H. C.

*Graphite compound [lubricant] and process of making it*. G. Kirkegaard, Brooklyn, N.Y., Assignor to National Graphite Lubrication Co., Wilmington, Del. U.S. Pat. 1,185,682, June 6, 1916. Date of appl., Feb. 12, 1913.

A NORMALLY solid lubricant is formed by mixing finely divided flocculent graphite with a partially carbonised resinous (shellac) binder.—W. H. C.

*Lubricants; Method of making*—. C. H. Bierbaum, Buffalo, N.Y. U.S. Pat. 1,186,167, June 6, 1916. Date of appl., Mar. 30, 1914.

GRAPHITE is ground in a dilute solution of asphaltum, and the mixture is diluted with lubricating oil.—W. F. F.

*Liquid-heater; Centrifugal*—. H. Feldmeier, Assignor to D. H. Burrell and Co., Little Falls, N.Y. U.S. Pat. 1,186,175, June 6, 1916. Date of appl., May 23, 1912.

A CYLINDRICAL vessel with its axis slightly inclined to the vertical is mounted on a frame and provided with a rotating paddle, while it is surrounded by a heating jacket and by an outer air jacket. These jackets are connected at their ends to annular heads, one of which is mounted so as to slide on the heating vessel. Liquid to be heated enters at the bottom and is delivered at the top into an enlargement of the heating vessel provided with an enlarged extension of the rotating paddle. The heated liquid is finally delivered through an opening in the side of the larger chamber.—W. F. F.

*Filter for liquids, especially for sugar juices*. Pfeifer und Langen Ges. m. b. H., Elsdorf. Ger. Pat. 291,519, Dec. 23, 1914.

FILTER-CLOTH woven from paper yarn is used: two or more layers of the paper yarn cloth may be

used or a layer of paper yarn cloth having a layer of cellulose or paper pulp firmly united to it. Filtration is more rapid than with a filter-cloth made of hemp or jute, a clear filtrate is obtained, and, especially in the filtration of sugar juices, the pores of the cloth are not clogged so quickly.—A. S.

*Liquefaction and separation of gases; Expansion apparatus for the*—. R. Mewes, Berlin. Ger. Pat. 291,751, Oct. 29, 1912.

A NARROW clearance space is left between the piston and the wall of the cylinder in which the gaseous mixture is compressed. The use of lubricants is thus rendered unnecessary, and the small quantity of compressed gas which passes through the clearance space to the space behind the piston produces cold by its expansion and thus performs useful work.—A. S.

*Thermochemical reactions in closed vessels; Utilisation of combustible gases produced by— as heating agent in the process*. Siemens und Halske A.-G., Siemensstadt. Ger. Pat. 291,782, July 13, 1913.

THE gases are burnt by means of surface combustion in a mass of refractory material surrounding the reaction chamber.—A. S.

*Fires; Process for quenching— by means of steam and water under pressure*. F. Adedter, Hamburg. Ger. Pat. 291,788, Apr. 3, 1914. Addition to Ger. Pat. 291,380 (this J., 1916, 681).

THE quenching agent consists of steam under considerable pressure, which, immediately before use, is mixed with so much water under pressure, that a mist of relatively low temperature is produced. In a space of 1000 cb.m. the strongest fire can be quenched in 3–5 mins. by means of the mist produced from 20 kilos. of steam of 16 atmospheres pressure and 850 kilos. of water, without the use of flame-extinguishing gases, such as carbon dioxide, etc.—A. S.

*Centrifugal separator*. Jahn und Co., Arnswalde. Ger. Pat. 291,930, Feb. 27, 1914.

AN inner perforated cylindrical drum and an outer non-perforated tapering drum are rotated at different speeds. The solids separated from the material under treatment are moved towards a discharge opening at the smaller end of the tapering drum by conveyor-blades mounted on the outside of the cylindrical drum and on a cylinder rotating inside the latter. Rollers movable freely in a radial direction are forced against the inner surface of the perforated drum and press the material which separates thereon, and channels are provided by which the material separated in the inner drum can pass into the field of action of the conveyor-blades in the outer tapering drum.—A. S.

*Inflammable liquids; Storage plant for*—. A. Beretta, Milan, Italy, Assignor to Martini und Hünke Maschinenbau A.-G., Berlin. U.S. Pat. 1,186,269, June 6, 1916. Date of appl., Sept. 30, 1913.

SEE Eng. Pat. 22,400 of 1913; this J., 1914, 64.

*Mill with grinding ring*. E. Bouvier, Niederuzwil, Assignor to Gehr. Bühler, Uzwil, Switzerland. U.S. Pat. 1,187,246, June 13, 1916. Date of appl., Dec. 4, 1914.

SEE Eng. Pat. 24,120 of 1914; this J., 1916, 344.

## IIA.—FUEL; GAS; MINERAL OILS AND WAXES.

*Pitch; Carbonisation of*—. E. W. Smith. Midland Junior Gas Assoc., June 24, 1916. J. Gas Lighting, 1916, 124, 687–689.

TABLES are given showing the results obtained by





sides, down which it flows in a thin film. Other conical plates maintain the flow in the desired direction until it reaches the outlet at the bottom. The vapours are conducted into a vertical column and thence to the condensers. The plant is suitable either for "topping" or for complete distillation. When 60 to 70% of the crude oil, comprising all the benzene, kerosene, and intermediate fractions, is to be removed, a series of connected continuous cylindrical stills is commonly used. These range from about 19 to 30 ft. in length by 7 to 10 ft. in diameter, and are fitted with internal flues to increase the heating surface, and have preheaters both for the distillates and residue. The benzene is redistilled in stills heated by means of superheated steam passed through coils, while the kerosene is redistilled in stills of the same kind as those used for the crude oil. The heavy oil is either distilled to yield lubricants or concentrated to yield residues. To prevent "cracking," the stills are connected with a vacuum pump. *Extraction of paraffin wax.*—The oil containing the wax is cooled first naturally and then by means of refrigerators using liquefied ammonia or carbon dioxide. Cooling is applied in one or two stages according to the amount of paraffin wax in the oil and the temperature at which a bright filtrate is obtained. Slow cooling, as in apparatus cooled by circulating brine, tends to effect better crystallisation of the wax than the more rapid cooling by direct action of a refrigerating agent. The crude wax is separated from the frozen mass by pumping it through filter-presses giving a pressure up to 150 lb. per sq. in., and which are worked in a room chilled by brine pipes suspended from the ceiling. In another process of separation, patented by the Triester Mineralöl Raffinerie, the fluid mixture of oil and wax is cooled down uniformly with only sufficient motion to prevent the formation of a non-conducting coating on the vessel. This motion is provided by the movement of a skeleton scraper round the interior of the vessel, which is meanwhile cooled outside by a current of water. The paraffin is precipitated on a false bottom of gauze, through which the sweated oil readily passes. *Refining of paraffin wax.*—In Henderson's sweating plant the wax is sweated in upright cylinders of sheet iron, 9 ft. high by 17 in. in diameter, within which other cylinders 7 in. in diameter are fixed. The latter are open at top and bottom, and the annular space between them and the outer cylinders is fitted with a false bottom of gauze a little above the outlet cock, while wire gauze is placed in layers round the inner cylinder. The wire gauze acts as a wick in drawing off the "sweats" and the process may be assisted by the suction of a steam injector. In Pyzel's plant the sweating vessels are placed on trucks which pass progressively through a passage heated by means of air blown over a hot coil. The finished wax is melted in the outlet air sluice. After sweating, the wax is freed from final traces of colouring matter by treatment with a decolorising medium, especially bauxite, which has also proved efficacious for decolorising and deodorising lamp oils and lubricants. The wax is best brought into contact with the bauxite by filtration, and all free moisture should be eliminated from both wax and bauxite. After the decolorisation, wax still adhering to the bauxite is extracted with petrol, the solvent expelled from the residue by steaming, and the bauxite incinerated and used again. The decolorised wax is passed through filter paper (e.g., in Bryson's filter) on its way to the cooling racks. *Chemical treatment.*—A method of treating petrol is to pass it with a minimum of disturbance through vertical vessels containing the chemicals, the reactions taking place as well as when agitation is used and with but little loss of spirit. Kerosene is agitated with compressed air in large washers, while in the case of lubricants the

same process is used in small vessels not exceeding 100 barrels in capacity. In Edeleanu's process (this J., 1914, 343), the liquid sulphurous acid dissolves the sulphur-containing constituents of the oil, and thus eliminates the objectionable odour of distillates which contain sulphur compounds. For example, a kerosene distillate containing 0.6% of sulphur showed only 0.08% after the treatment, while in another sample the sulphur was reduced from 0.46% to 0.04%. Deodorisation may also be effected by treating the distillates with an alkaline solution of litharge, prior to treatment with sulphuric acid. *Candle manufacture.*—The paraffin wax is melted by means of steam and mixed with a small proportion of stearine, and the mixture is clarified by means of oxalic acid, which precipitates any calcium salts present. The supernatant wax is run into a steam-jacketed pan, where impurities are readily detected. Thence it is transferred by means of a "swimmer" to a "jack" or bucket, which delivers a regular stream of melted material to the moulding machines. —C. A. M.

*Gasoline; Cost of making*—by the Rittman process. Min. and Eng. World, 1916, 44, 1132.

The following U.S. Government estimates are based on the results of a 5-days run with an apparatus provided with five cracking tubes, each having a capacity of about 65 U.S. galls. per hour; allowing for stoppages, the total working capacity is 5000 barrels (1 barrel=42 U.S. galls.) per month. The yield of gasoline is about 17% and the loss 10%, whilst the residue consists of fuel oil equal in value to the fuel oil used as raw material. The cost of the plant is estimated as \$15,000 and of the building as \$5000. Using fuel oil at 50 cents. per barrel (42 U.S. galls.), the cost of production of gasoline is estimated as follows:—

5000 barrels fuel oil .....	\$2500
Labour .....	560
Fuel .....	160
Electricity .....	100
Repairs .....	100
Interest and depreciation, 6% each .....	200
Refining cost, 20 cents per barrel .....	1000
Total cost .....	\$4620
Residue, 3650 barrels at 50 cents per barrel .....	1825
Net cost of 850 barrels of gasoline .....	\$2795

= 7.8 cents per gallon of gasoline.

In a similar way, the cost of gasoline is estimated as 9.74 cents per gallon with fuel oil at \$1 per barrel, 11.5 cents per gall. with fuel oil at \$1.47 per barrel, and 13.9 cents per gallon with fuel oil at \$2.10 per barrel.—A. S.

*Gasoline; Extraction of*—from natural gas by absorption methods. G. A. Burrell, P. M. Biddison, and G. G. Oberfell. Natural Gas Assoc. of America, May 15, 1916. Met. and Chem. Eng., 1916, 14, 651—660.

Most of the so-called "dry" natural gases contain 1 to 2 pints of gasoline per 1000 cub. ft., and while this amount is too small to be recovered by compression and condensation methods (see this J., 1915, 1044), it may be profitably dealt with by an absorption method similar to the process of extracting benzene and toluene from coke-oven gases, except that the natural gas has to be treated at the pressure at which it is transported, viz., 200 to 300 lb. per sq. in. The removal of gasoline from "dry" gas is also important on account of the solvent action of condensed gasoline on the rubber rings used in the pipe couplings of the trunk lines, involving a large consumption of rubber and loss of gas through resulting leaks. It is considered that by absorption methods 75,000,000 gallons of gasoline, at present unrecovered, may be obtained annually. Tests were

made with an experimental plant having a capacity of 15,000 to 30,000 cub.ft. per hour. The absorbing oil was a mineral seal oil from which the dissolved gasoline was recovered by steam distillation, the oil then being cooled and pumped back to the absorber. This oil had sp.gr. 0.850 (water=1) and flash point (Pensky-Martens closed apparatus) 135° C. The best results were obtained by using a stone tower absorber in which the oil flowed down over a column of stones and the gas ascended. It was necessary with this tower to circulate 4 gallons of oil per 1000 cub.ft. of gas. In the case of the two gases dealt with in the experimental plant, the heating value was lowered 3.8% and 2.4% respectively by the extraction of the gasoline; the one gas contained 1.5 and the other 1 pint of gasoline per 1000 cub.ft. The sp.gr. of the gasoline obtained varied between 77° and 85° B. (sp.gr. 0.651 and 0.676). The boiling points ranged from 80° F. (26.7° C.) to 300° F. (149° C.). The evaporation loss was about 11% in 24 hours as compared with an evaporation loss of about 2.4% in 24 hours of a straight refinery gasoline of 60.4° B. (sp.gr. 0.735). The vapour pressure of the gasoline ranged from 1 lb. per sq. in. at 70° F. (21° C.) to about 5 lb. at 100° F. (38° C.). This latter value is of importance as enabling the gasoline, under U.S. regulations, to be transported in tank cars, the specified maximum being 10 lb. per sq. in. at 100° F. (38° C.). It is estimated that a plant capable of handling daily 60,000,000 cub.ft. of gas yielding 1 pint of gasoline per 1000 cub. ft., would cost \$60,000. The gasoline obtained would realise \$1500 daily, at 20 cents per gallon. Tests were also made in which the natural gas was simply passed into a naphtha of about 55° B. (sp.gr. 0.757), the product in this case being at once a commercial article requiring no further treatment. When the naphtha had absorbed all the gasoline that was desired, it was removed and fresh naphtha substituted. By this scheme there were obtained yields of gasoline varying between 300% and 500% greater than by the oil absorption and distillation method. An objection to the process lies in the fact that a large amount of naphtha has to be handled—at least seven times the volume of the gasoline recovered.—T. St.

*Petroleum spirit; Discharge in earthed receptacles containing*—which has been electrically charged through flowing through narrow tubes. D. Holde. Z. Elektrochem., 1916, 22, 195—199. (See also this J., 1915, 649; 1916, 411.)

THE extreme mobility of the molecules of fluid insulators causes them almost instantaneously to give up to the containing vessel any charge which they may have acquired in flowing through narrow tubes or pipes. Although theoretically, therefore, petroleum spirit, having a conductivity of  $10^{-14}$ — $10^{-15}$  would take, if perfectly motionless, 39—390 seconds to discharge say from 3000 volts down to 300 volts, yet in practice any danger of a spark discharge is quite excluded owing to the motion of the liquid, provided the pipes and walls of the receptacles are well earthed. Even in the most unfavourable cases the addition of a small quantity of acetic acid (0.1%) or alcohol would increase the conductivity to above  $3 \times 10^{-13}$  when even by conductivity alone the discharge would take place in less than a second.—G. F. M.

*Automobile cylinder oils; Data on the oxidation of*—C. E. Waters. U.S. Bureau of Standards, Technol. Paper No. 73. J. Franklin Inst., 1916, 181, 850—851. (See this J., 1911, 608, 1367; 1913, 1000.)

ON exposure to sunlight and air for 438 hours the rate of increase of weight due to oxidation gradu-

ally diminishes, and the formation of acid and the carbonisation value increase more rapidly. The Maumené number increases rapidly as the result of oxidation but the iodine number is lowered. The oxidised oils emulsify readily when agitated with water, but filtration through animal charcoal removes the emulsifying agents. When the oils are heated at 250° C. for one to seven hours or for three hours at 230°—280° C., carbonised matter forms at a rapidly increasing rate. The greater the rate of carbonisation at lower temperatures the more rapidly does it increase at higher temperatures or on prolonged heating. It is, therefore, unnecessary to prolong the heating in testing these oils. The carbonisation value is independent of the flash- and fire-points and of the loss from evaporation on heating.—A. B. S.

*Petroleum products; Oxidation of*—B. Schreyer and S. Kragen. Petroleum, 1916, 11, 521—522. Z. angew. Chem., 1916, 29, Ref., 294.

BY the oxidation of different petroleum fractions by air in presence of finely powdered dry sodium hydroxide and mercury, yields of 1—1.5% of naphthenic acids were obtained in the form of viscous liquids of characteristic odour and red colour with green fluorescence. The residual petroleum had a high specific gravity owing to the presence of other oxidation products. These were removed by extraction with hot 75—80% alcohol whilst agitating with air, and were obtained in the form of a yellow, fairly viscous oil, having a pleasant ethereal odour. The oil is easily soluble in organic solvents, and consists of a tertiary unsaturated alcohol.—A. S.

*Production of aromatic hydrocarbons from paraffin wax.* Egloff and Twomey. See III.

*Composition of carburetted water-gas tar.* Brunkow. See III.

*Heat treatment of steel in coal gas.* Walter. See X.

*Determination of iodine and bromine in saline waters from petroleum-bearing strata.* Popa. See XIXB.

#### PATENTS.

*Fuel [briquettes].* E. R. Sutcliffe, Leigh, and Pure Coal Briquettes Ltd., Cardiff. Eng. Pat. 5018, Mar. 31, 1915.

CARBONACEOUS substances such as coal, anthracite, coke, or charcoal, are reduced to a very finely divided state, and in those cases where it is requisite, a binding material is added to the dust before it is compressed into blocks or briquettes. The briquettes are then heated at such a temperature and for such a time as is required by the character and purpose to which the coke residue, or the by-products, are to be applied. A mixture of 75% anthracite, 15% steam coal, and 10% dry pitchish stated to yield an excellent fuel when briquetted in this way. It is necessary however to roast the anthracite in a retort in the absence of air at a temperature of 300° to 700° C. before admixture with the other components of the briquette.

—J. B. C. K.

*Fuel; Manufacture of composition*—C. T. Hopkins, Walthamstow, Essex. Eng. Pat. 14,771, Oct. 19, 1915.

A MIXTURE of fine coal or coal and cinders in the proportion of 2:1, 16 lb., soot 8 lb., with or without wheat flour 0.25 lb., is mixed with water 3 pints, with or without sodium carbonate 1 oz. The mixture is moulded under pressure or worked by hand into spherical masses.—W. F. F.

*Fuel from anthracite duff or small coal; Manufacture of* —. D. P. Lloyd and T. H. Jolley, Ammanford, Carmarthen. Eng. Pat. 100,547, Jan. 11, 1916. (Appl. No. 450 of 1916.)

A MIXTURE of anthracite duff or small coal 1—1.25 tons, lime or cement 1 cwt., and salt 2—4 lb., is moistened, and moulded in steam-heated moulds coated or lubricated with pitch.—W. F. F.

*Briquetting with crude naphthalene; Plant for* —. J. Efrém, Woltersdorf. Ger. Pat. 292,454, Oct. 4, 1913.

THE crude naphthalene is melted in a closed chamber, and then led to nozzles which distribute it over the material to be briquetted; on its way it passes through a heating chamber, in which it is retained for such a period that about one-fifth of its weight sublimes; a cooled chamber is provided to collect the sublimed naphthalene. If the fraction of crude naphthalene which melts at about 70° C. is used, the residue which leaves the intermediate heating chamber remains liquid at about 40° C., at which temperature it can be mixed with the material to be briquetted, without any evolution of naphthalene vapour.—A. S.

*Fuels; Method of drying moist — by addition of quicklime.* E. Schimansky, Berlin. Ger. Pat. 292,541, July 31, 1915.

THE fuel is partially dried, then mixed with quicklime, and pressed, the ratio of water to lime in the mixture being such that the lime is completely slaked and the heat generated is sufficient to vaporise the remaining water.—A. S.

*Coal for coking; Process for compacting and dehydrating* —. E. Pohl, Rhöndorf. Ger. Pat. 292,530, May 19, 1915.

CONSOLIDATION and dehydration of the coal is effected by shaking or jolting in a shaking machine; during the operation a weighted plate is placed on the surface of the coal to consolidate the surface layer.—A. S.

*Coke-ovens; Method of heating* —. C. Otto und Co. G.m.b.H., Dahlhausen. Ger. Pat. 292,142, July 2, 1915.

TO attain uniform heating over the whole of the heating wall, mixtures containing excess of air and of gas respectively are burnt in alternate heating flues, and in the upper part of the flues the excess of gas from one set of flues is burnt by means of the excess of air from the other set.—A. S.

*Coke-oven.* A. E. Peters, Westmont Borough. Pa. U.S. Pat. 1,183,401, May 16, 1916. Date of appl., Sept. 10, 1913.

THE oven is provided in the side walls with a large number of double heating flues of inverted U-form, the mixing chamber for gas and air being connected with the lower ends of one of each pair of legs. A fuel-gas and hot-air supply is connected with the mixing chambers, and means are provided for reversing the direction of the flow of the gases through the heating flues and mixing chamber as desired.—J. B. C. K.

*Coke; Method of improving — for use as domestic fuel.* A. Schollenbruch, Düsseldorf. Ger. Pat. 291,568, July 23, 1915.

THE coke is impregnated with a thin paste of water, coal dust, and loam or the like, then coated with a thick paste of the same materials, and dried; dry coal dust is sprinkled over it towards the end of the drying process.—A. S.

*Sulphur-bearing fuel and other substances; Compound for treating* —. C. Foxwell, Assignor to The Smoke-Coal Economizer Corporation, Baltimore, Md. U.S. Pat. 1,183,445, May 16, 1916. Date of appl., Feb. 19, 1916.

THE fuel is treated before burning with a solution of calcium chloride and borax, containing boron and chlorine in the proportions represented by BCl<sub>3</sub>.—J. B. C. K.

*Gas; Manufacture [and testing] of* —. L. H. Eady and H. W. Clarke, Southampton. Eng. Pat. 8830, June 15, 1915.

GAS is drawn from a point between the retorts and exhaustor by a water-jet pump and passed through a cooler, filter, and governor to a jet photometer or the like. The retort-house governor bell carries a water tank, into which the short leg of a siphon dips. The long leg of the siphon has two branches with valves, one connected with a water supply and the other to waste. These valves are manipulated so as to add to or withdraw from the water in the tank on the governor bell while the photometer flame is kept steady, and thus the gas is maintained at uniform quality.—W. F. F.

*[Gas] retorts; Revolvable* —. W. Thomas, Nanaimo, B.C., Canada. Eng. Pat. 9156, June 22, 1915.

A HORIZONTAL revolving gas-fired retort for coal distillation is provided with long combustion passages in the walls, into which open a number of Bunsen burners. The coal is fed in at one end by a helical conveyor in a projecting neck of the retort and the longitudinal gas-supply pipes for the Bunsen burners are connected to an annular groove in the projecting neck, which is surrounded by a fixed collar into which the gas is led.—W. F. F.

*Gas; Method of making combustible —. Method of carbonising fuel [coal] in vertical-retort gas-benches for the production of gas and carbonised fuel [coke]. Method of conducting combustion.* H. L. Doherty, New York. U.S. Pats. (A) 1,187,048, (B) 1,187,049, (C) 1,187,050, and (D) 1,187,051, June 13, 1916. Dates of appl., Nov. 15, 1911; (A), (B), and (C) renewed Apr. 28, 1916.

(A) A BODY of fuel is conveyed, at a rate greater than that of complete combustion, past an oxidising current of such nature and in such volume that part of the fuel is converted into combustible gas. Part of this gas is circulated through the unburnt fuel and then through the partly burnt fuel to cool the latter, and is then withdrawn with the main current of combustible gas. The coarser part of the cooled fuel is separated and mixed with a regulated portion of fresh fuel for use as above. (B) Coal or a mixture of coal and coke is passed through a relatively long conduit heated externally at its middle zone, and the gas is withdrawn through the fuel at the charging end, where the heavier distillation products are condensed in the fuel. Part of the gas is treated to remove illuminants, cooled, and passed through the withdrawal end of the retort to cool the coke, and then returned to the gases leaving the charging end of the retort. (C) In a retort such as that described in (B), air is supplied to the heated zone in quantity sufficient to maintain the fuel at the desired temperature. Part of the discharged coke is mixed with the fresh coal charged into the retort to maintain its porosity. (D) In a retort such as that described in (C), a portion of the gas from the combustion zone is passed through the advancing fuel to preheat it and cool the gas, and the gas is then passed through the fuel at the discharge end to cool it and heat the gas, which is

then passed through the combustion zone. The rate of feeding of the fuel by gravity may be such that sufficient fuel remains unburnt to maintain the porosity of the charge in the retort.—W. F. F.

*Distillation; Process of and apparatus for*—. [Recovery of pentane from gasoline.] W. O. Snelling, Pittsburgh, Pa. U.S. Pat. 1,186,855, June 13, 1916. Date of appl., Sept. 28, 1914.

To recover volatile components from petroleum oils, the oil is passed successively through a series of vaporisers and condensers at temperatures which progressively approach each other and approach the boiling point of the component to be recovered, the uncondensed vapour being removed at each stage. When applied to the recovery of normal pentane from gasoline, the vapour is passed through a condenser at 27° C., and the condensed liquid passed successively through vaporisers and condensers at 47° C. and 32° C., and finally at 42° C. and 35° C.—W. F. F.

*Petroleum residues; Process of treating*—. C. S. Palmer, Upper Montclair, N.J. U.S. Pat. 1,187,380, June 13, 1916. Date of appl., Mar. 2, 1907.

THE yield of volatile compounds from petroleum residues is increased by digesting the residues under pressure of the evolved vapour between 60 and 400 lb. per sq. in. and at a temperature above 200° C. but below the point at which substantial carbonisation occurs, and without the addition of steam. The heating is continued till the greater part of the residue is converted into more volatile compounds, which are separated when the pressure is relieved.—W. F. F.

*Hydrocarbons; Process of producing low-boiling*—. E. C. R. Marks, London. From Iroline Co. of America, Wilmington, Del., U.S.A. Eng. Pat. 3327, Mar. 2, 1915.

LOW-BOILING hydrocarbons suitable as fuel for internal combustion engines are obtained by heating liquid or fusible hydrocarbons of higher boiling point in a closed vessel to a temperature sufficient to develop a pressure of 200–500 lb. per sq. in., the volume of hydrocarbon being from 0.125 to 0.5 that of the vessel. The liquid is withdrawn under sufficient pressure to retain the low-boiling hydrocarbons in solution at a lower temperature and these are recovered by distillation. (Reference is directed in pursuance of Sect. 7, Sub-sect. 4, of the Patents and Designs Act, 1907, to Eng. Pat. 18,419 of 1914, this J., 1915, 1045.)—W. F. F.

*Combustion or power liquids; Method for manufacturing*—. J. N. Wingett, Assignor to W. A. Haggott, Denver, Colo. U.S. Pat. 1,185,747, June 6, 1916. Date of appl., Mar. 1, 1915.

LIQUID hydrocarbon, such as kerosene, is mixed with toluene and a nitrating solution, and the mixture distilled.—W. F. F.

*Artificial fuel; Furnace for the preparation of*—. V. Groom, London. U.S. Pat. 1,187,305, June 13, 1916. Date of appl., Apr. 24, 1916.

SEE Eng. Pat. 24,085 of 1914; this J., 1916, 103.

*Coke-oven*. N. Schuster, London. U.S. Pat. 1,186,687, June 13, 1916. Date of appl., Dec. 21, 1914.

SEE Eng. Pat. 29,494 of 1913; this J., 1914, 684.

*Coke-oven; Regenerative*—. C. Wilke, Assignor to C. Still, Recklinghausen, Germany. U.S. Pat. 1,185,961, June 6, 1916. Date of appl., June 11, 1914.

SEE Ger. Pat. 271,515 of 1913; this J., 1914, 471.

*Gas retorts; Settings of*—. H. A. Carpenter, Sewickley, Pa., and Ritter-Conley Manufacturing Co., Leedsdale, Pa., U.S.A. Eng. Pat. 100,028, June 8, 1915. (Appl. No. 4130 of 1916.)

SEE U.S. Pats. 1,174,390 and 1,177,171 of 1916; this J., 1916, 527, 592.

*Oil-gas; Process for manufacturing*—. B. van Steenberg, New York. Eng. Pat. 9155, June 22, 1915.

SEE U.S. Pat. 1,124,364 of 1915; this J., 1915, 216.

*Volatile composition suitable [as fuel] for explosion-engines; Process of making a stable*—. W. R. Gulick, Jersey City, N.J. U.S. Pat. 1,187,061, June 13, 1916. Date of appl., July 31, 1913.

SEE Eng. Pat. 18,681 of 1913; this J., 1914, 244.

*Gas and liquid coolers and gas scrubbers*. Eng. Pat. 8762. See I.

*Industrial gas burners and furnaces*. Eng. Pat. 100,603. See I.

*Treatment of waste sulphuric acid from the refining of tar oils or petroleum*. Ger. Pat. 291,775. See III.

*Treatment of sulphuric acid residues from petroleum refining*. U.S. Pat. 1,186,373. See VII.

*Gas analysing apparatus*. U.S. Pat. 1,186,014. See XXIII.

## IIB.—DESTRUCTIVE DISTILLATION; HEATING; LIGHTING.

### PATENTS.

[Arc-lamp] *projector-carbon*. W. G. Wilcox, Lakewood, Ohio, Assignor to National Carbon Co., Cleveland, Ohio. U.S. Pat. 1,186,253, June 6, 1916. Date of appl., July 2, 1913.

A MIXTURE of 19–10 parts of potassium silicate and 1–10 parts of potassium silicofluoride, alone or mixed with carbon, is used to form a core for projector carbons for arc lamps.—W. F. F.

*Ultraviolet radiation; Apparatus for producing*—. F. G. Keyes, Boston, Mass., Assignor to Cooper Hewitt Electric Co., Hoboken, N.J. U.S. Pat. 1,186,993, June 13, 1916. Date of appl., July 1, 1913.

TWO chambers, containing hydrogen at different pressures, are separated by a mercury trap and a cock, so that a portion of the gas may be withdrawn from the chamber of lower pressure by suitable means, and successively replaced from the higher pressure supply chamber.—B. N.

*Electron emitting cathodes and process of manufacturing the same*. A. McL. Nicolson, New York, and E. C. Hull, Montclair, N.J. Eng. Pat. 17,580, Dec. 16, 1915. Under Int. Conv., Dec. 26, 1914.

SEVERAL successive coatings of strontium hydroxide are applied to the metallic filament, and afterwards similar coatings of barium resinate. The process is repeated, and the filament then heated to ignition temperature, thus producing alternate superposed films of barium and strontium oxides.—B. N.

*Arc-lamp electrode*. M. Doetsch, Assignor to C. Conradty, Nuremberg, Germany. U.S. Pat. 1,187,282, June 13, 1916. Date of appl., Dec. 17, 1913.

SEE Eng. Pat. 22,223 of 1913; this J., 1914, 913.

*Treatment of sewage sludge and the like*. Eng. Pats. 3355 and 10,262. See XIXb.

## III.—TAR AND TAR PRODUCTS.

*Carburetted water-gas tar; Composition of —.*  
H. K. Brunkow. J. Gas Lighting, 1916, 135, 67.

TAR from a carburetted water-gas plant generated at somewhat higher temperatures than ordinary, and using Californian crude oil of 18.8° B. (sp.gr. 0.941), after passing through a settling apparatus had a sp.gr. of 1.026 at 95° F. (35° C.). It consisted of about 60% of water, 10% of lampblack, 26% of heavy oil, and 4½% of naphthalene. It was nearly saturated with naphthalene and was useless as an absorbent of benzol or light oil.

—W. H. C.

*Aromatic hydrocarbons from paraffin wax; Production of —.* G. Egloff and T. J. Twomey. J. Phys. Chem., 1916, 20, 515—521.

HITHERTO only aliphatic hydrocarbons have been obtained by the cracking of paraffin wax, and the production of aromatic hydrocarbons by the cracking of petroleum has been ascribed by Brooks (this J., 1915, 412) to the presence of compounds containing the phenyl radicle in the petroleum. The authors' experiments were made on a sample of commercial paraffin wax of m.pt. 47° C., containing 0.05% oil, and the vapour cracking apparatus described previously (see this J., 1915, 1199) was used. No aromatic hydrocarbons were produced at atmospheric pressure and 500° C., but benzene, toluene, and xylene were formed at 600° C. at atmospheric pressure and at 500° and 600° C. at 150 lb. pressure. At 600° C. and 150 lb. pressure the oil produced by cracking contained 6.6% benzene, 5.4% toluene, and 2.3% xylene, or 2.6, 2.2, and 0.9% respectively on the quantity of paraffin wax.—A. S.

*Nitro-compounds; Chemical processes in the reduction of aromatic — to amino-compounds on the large scale.* P. N. Raikow. Z. angew. Chem., 1916, 29, 239—240. (See also this J., 1916, 627.)

THE "activating" influence of salts of the heavy metals on the action of metals on water owing to their hydrolytic decomposition, is the underlying principle of the reduction of aromatic nitro-compounds by means of iron and water and a trace of hydrochloric acid. The ferrous chloride generated initially by the action of the iron on the acid is hydrolysed by the water and the hydrolytic equilibrium is disturbed by the removal of the free acid by reaction with a further quantity of iron, with the generation of hydrogen and reproduction of ferrous chloride, thereby completing the cycle, which is repeated so long as iron and water are present. The complete changes are expressed by the scheme:  $3\text{Fe} + 6\text{HCl} + \text{C}_6\text{H}_5\text{NO}_2 = 3\text{FeCl}_2 + 2\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{NH}_2$ , and  $3\text{FeCl}_2 + 3\text{H}_2\text{O} \rightarrow [3\text{Fe}(\text{OH})_2 + 6\text{HCl}] + 3\text{Fe} + \text{C}_6\text{H}_5\text{NO}_2 \rightarrow 3\text{Fe}(\text{OH})_2 + 3\text{FeCl}_2 + 2\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{NH}_2$ . The explanation of Muspratt previously given must accordingly be modified to the extent that the reaction depends primarily on the hydrolytic decomposition of ferrous chloride by water, whilst the formation of aniline hydrochloride and its reaction with iron is subsidiary and incidental.

—G. F. M.

*Systems in which water, a phenol, and a base constitute the components; Equilibria in —.* G. J. van Meurs. Z. physik. Chem., 1916, 91, 313—346. J. Chem. Soc., 1916, 110, ii., 304—305.

THE heterogeneous equilibria between phenol, water, and each of the bases, sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, barium hydroxide, and strontium hydroxide have been investigated at 25° C.; similar measurements have been made for the systems water, resorcinol, and each of the bases

potassium hydroxide and barium hydroxide at 30° C. The three components in varying quantities were shaken in a thermostat until the required equilibrium had been set up; the solid and the liquid phases were then analysed. The experimental results are expressed in tabular form and also in curves. The first-named six systems exhibit a binodal curve. All the systems examined show isotherms made up of several curves, and these represent solutions which at the experimental temperature are saturated with the solid phase. The following substances occur as solid phases in one or other of the systems examined:

$\text{C}_6\text{H}_5\text{OK} \cdot 2\text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_5\text{ONa} \cdot 3\text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_5\text{OLi} \cdot 2\text{H}_2\text{O}$ ;  $(\text{C}_6\text{H}_5\text{O})_2\text{Ca} \cdot 3\text{H}_2\text{O}$ ;  $(\text{C}_6\text{H}_5\text{O})_2\text{Ba} \cdot 4\text{H}_2\text{O}$ ;  $(\text{C}_6\text{H}_5\text{O})_2\text{Sr} \cdot 4\text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_5\text{ONa} \cdot 2\text{C}_6\text{H}_5\text{OH}$ ; and  $\text{C}_6\text{H}_5\text{OK} \cdot 3\text{C}_6\text{H}_5\text{OH}$  at 25° C., and  $\text{C}_6\text{H}_5\text{H}(\text{OK})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_5\text{O}_2\text{Ba} \cdot 2\text{H}_2\text{O}$  (?), and  $\text{HO} \cdot \text{C}_6\text{H}_4\text{OK} \cdot 2\text{H}_2\text{O}$  at 30° C. All the compounds mentioned above are soluble in water without decomposition. Tables of solubilities of these substances at the indicated temperatures are given. From the curves it is seen that by the addition of a base to an aqueous phenol solution, the phenol is eventually to a very large extent thrown out of the solution as phenoxide. On comparing the composition of the boundary solutions, that is, solutions which are saturated with phenol and base, with one another, and with a saturated solution of phenol in water, it is seen that the phenol content is much less in alkali solutions than in water, the values being: water, 93.78%; potassium hydroxide, 0.12%; sodium hydroxide, 0.32%; lithium hydroxide, 2.03%; calcium hydroxide, 12.05%; barium hydroxide, 12.65%; and strontium hydroxide, 22.32%. In the solutions of the alkalis the phenol content increases as the content of alkali decreases, whereas with the alkaline earths both phenol and base increase together. The mono-acid bases expel more phenol from solutions than the di-acid bases. At the same time, the incorrectness of the text-book statement, "that phenol is easily soluble in alkali hydroxides," is demonstrated.

*Hydrogen peroxide as a hydrolytic agent.* J. V. Dubsky. J. prakt. Chem., 1916, 93, 137—142.

HYDROGEN peroxide behaves towards cyanides as a hydrolytic agent converting them into amides according to the equation:  $\text{R} \cdot \text{CN} + 2\text{H}_2\text{O}_2 = \text{R} \cdot \text{CONH}_2 + \text{O}_2 + \text{H}_2\text{O}$  (compare Radziszewski, Ber., 1885, 18, 355). Although not proceeding with equal facility in all cases, the reaction can be brought about with cyanides, which had previously been found to resist the action of hydrogen peroxide, by using a large excess. Thus, 2.5 grms. of *o*-tolunitrile in 50 c.c. of methyl alcohol gave a yield of 2.1 grms. of *o*-toluamide on treatment at 40°—60° C. with 200 c.c. of 3% peroxide and 10 c.c. of *N*/1 sodium hydroxide, the reaction product being subsequently neutralised, evaporated to dryness, and extracted with alcohol. Similar results were obtained with *a*-naphthonitrile, whilst with iminodipropionitrile, and iminodi-isobutyronitrile, small yields of amides were obtained. With diacetonitrile, on the other hand only a small quantity of a condensation product of this substance with aldehyde, produced from the alcoholic solvent, namely, 2,4,6-trimethyl-3,5-dicyanodihydropyridine, could be isolated. Potassium ferricyanide was converted by hydrogen peroxide into an isomeric modification which gives in water an intense brown red solution.—G. F. M.

*Carbonisation of pitch.* Smith. See IIA.

## PATENTS.

*Sulphuric acid from the refining of tar oils or petroleum; Treatment of waste —.* C. Still, Recklinghausen. Ger. Pat. 291,775, May 27, 1914.

THE waste acid is warmed and fed to a steam jet

blower worked by steam under pressure, which may be superheated. The intimate mixture of steam and waste acid thus produced is delivered to a vessel surmounted by a dome. The acid collects in this vessel, and the acid resins and other solid impurities settle out as a friable mass, which when freed from adhering liquid shows no sign of stickiness; the clear liquid acid is discharged through a tube. The steam and volatile substances after rising through the dome, which may be fitted with baffles to facilitate separation of liquid particles, pass to a condenser and then to a washer in which acid substances, such as sulphur dioxide, are absorbed; a steam jet injector is fitted in the pipe connecting the dome with the condenser in order to facilitate the flow of gases and vapours through the apparatus.—A. S.

2.9.10-*Trichloroanthracene*; *Manufacture of* —. Farb. vorm. Meister, Lucius, u. Brüning. Ger. Pat. 292,356, June 20, 1914.

ANTHRACENE or 9.10-dichloroanthracene is heated in a steam bath with sulphuryl chloride in presence of an indifferent solvent or diluent, e.g., nitrobenzene. On cooling, 2.9.10-trichloroanthracene separates; it is purified by crystallising from benzene.—A. S.

*Sulpho-chlorides of the naphthalene series*; *Manufacture of* —. Farb. vorm. Meister, Lucius, u. Brüning. Ger. Pat. 292,357, July 18, 1914.

SULPHO-CHLORIDES of the naphthalene series are obtained by treating acyl- $\beta$ -naphthylamines with chlorosulphonic acid. Acyl- $\alpha$ -naphthylamines, when treated in a similar manner, yield sulphonic acids.—A. S.

*Isatin*; *Manufacture of* —. Farb. vorm. Meister, Lucius, u. Brüning. Ger. Pat. 292,394, Aug. 11, 1914.

ISATIN is obtained by heating 3-amino-2.4-dihydroxyquinoline hydrochloride with ferric chloride solution. The dihydroxyquinoline can be prepared from anthranilic acid (Ger. Pats. 102,894 and 117,167), and the latter from phthalic acid, so that the new method affords a means of obtaining isatin cheaply from naphthalene.—A. S.

5-Nitro-1-alkylaminoanthraquinones; *Manufacture of* —. Farb. vorm. Meister, Lucius, u. Brüning. Ger. Pat. 292,395, May 7, 1914.

5-NITRO-1-ALKYLAMINOANTHRAQUINONES are prepared by nitrating  $\alpha$ -N-acidylalkylaminoanthraquinones.—A. S.

*Anthraquinone- $\alpha$ -mercaptans and disulphides*; *Manufacture of* —. Farb. vorm. Meister, Lucius, u. Brüning. Ger. Pat. 292,457, July 14, 1914.

ANTHRAQUINONE- $\alpha$ -SULPHOCHLORIDES or the corresponding sulphonic acids are reduced with hydro-sulphites.—A. S.

*Thioureas of the anthraquinone series*; *Manufacture of* —. Chem. Fabr. Griesheim-Elektron. Ger. Pat. 291,984, Dec. 19, 1914.

THIOUREAS of the anthraquinone series are prepared by heating 2-aminoanthraquinone or its ring-substitution products with an alkali xanthate in an organic solvent of high boiling point.—A. S.

*Diaminodiarlylketones and N-alkyl substituted diaminodiarlylthioketones*; *Manufacture of* —. J. Y. Johnson, London. From Badische Anilin und Soda Fabr., Ludwigshafen, Germany. Eng. Pat. 20,615, Oct. 6, 1914.

SEE Ger. Pats. 287,994 of 1913 and 289,108 of 1914; this J., 1916, 352, 353.

*Plant for briquetting with crude naphthalene*  
Ger. Pat. 292,454. See IIa.

#### IV.—COLOURING MATTERS AND DYES.

*Phenanthraquinone*; *Dyes derived from* —. K. C. Mukherjee and E. R. Watson. Chem. Soc. Trans., 1916, 109, 617–628.

ATTEMPTS to introduce additional hydroxyl groups into 2.7-dihydroxyphenanthraquinone, or 2-hydroxyphenanthraquinone, by treatment with manganese dioxide and sulphuric acid, or fuming sulphuric acid followed by fusion with potash gave no results of value, as apparently the phenanthraquinone molecule cannot withstand such treatment. From bromonitrophenanthraquinones, however, anilino-derivatives were obtained by Ullmann's method (Ber., 1901, 34, 2174), the nitro-groups being likewise replaced in some cases by the aniline residue. These products, which include 2.7-dianilino-, 2-, and 4-nitroanilino-, nitrodi-anilino- and dinitroanilino-phenanthraquinone, are all dyes giving dark green, blue, or black shades on wool (cp. Eng. Pat. 9311 of 1915; this J., 1915, 1136). Phenanthraquinone vat dyes were prepared by the action of acid chlorides on amino-phenanthraquinones. They are dissolved by alkaline hydrosulphite and reprecipitated on oxidation. Examples are 2-benzoylamino-phenanthraquinone which gives pale pink shades on cotton, 2-phthalylamino-phenanthraquinone giving pale yellow shades, and 2.7-dibenzoyldiamino-phenanthraquinone giving brownish-orange shades. Other derivatives prepared and examined as to their dyeing properties include 2.7-diamino-phenanthraquinonemonosulphonic acid, giving dull green shades on alum-mordanted wool, phenanthraquinone-2.7-bisazophenol, and certain more complex vat dyes obtained from dibromophenanthraquinone and 2-aminophenanthraquinone, *p*-phenylenediamine, and  $\beta$ -naphthylamine respectively. In the latter cases however the products were impure, and the dyes apparently of no great value.—G. F. M.

*Kermes*; *Dyesuff of* —. III. O. Dimroth and R. Fick. Annalen, 1916, 411, 315–338. (Compare this J., 1910, 749; 1914, 957.)

THE similarity in properties between hydroxyanthrapurpurin (1.3.4.6-tetrahydroxyanthraquinone) and decarboxylated kermesic acid proves conclusively that the latter is a derivative of the former. The colours of the alkaline solutions of hydroxyanthrapurpurin, decarboxylated kermesic acid, kermesic acid, and carminic acid are identical; the spectra of these solutions and the absorption spectra of solutions in sulphuric acid are similar, and dye-trials on wool and on mordanted cotton also show their relationship. Bromination of kermesic acid gives tribromococcin, and similarly bromination of hydroxyanthrapurpurin yields the tribromo-derivative. Reduction of kermesic acid with zinc dust and glacial acetic acid gives the leuco-compound of 1-methyl-3.5.8-trihydroxyanthraquinone; apparently kermesic acid loses, in addition to the acetyl and carboxyl groups, the  $\beta$ -hydroxyl group in the same manner that purpurin is reduced to quinizarin by this method. Kermesic acid is considered to be 1-methyl-4-carboxy-7-acetyl-3.5.6.8-tetrahydroxyanthraquinone. Carminic acid is reduced in the same manner, and the statements of C. and H. Liebermann (this J., 1914, 544) that it is not an anthraquinone derivative is considered incorrect.—F. W. A.

*Naphthoquinone derivatives*; *Degradation of hydroxyanthraquinones to* —. O. Dimroth and E. Schultze. Annalen, 1916, 411, 339–345.

AUTOXIDATION of anthragallol in alkaline solution

yields hydroxynaphthoquinonylacetic acid (Bamberger and Praetorius, *Monatsh. Chem.*, 1902, **23**, 688), but purpurin is degraded still further, giving phthalic acid on air oxidation in alkaline solution. Careful oxidation of carminic acid in alkaline solution by means of hydrogen peroxide using cobalt oxide as catalyst yields 8-methyl-2,6-dihydroxy-1,4-naphthoquinone-3,5-dicarboxylic acid (this J., 1914, 956), and on similar treatment purpurin gives 3-aceto-2-hydroxy-1,4-naphthoquinone. These results are explained by assuming that the position of the quinone group in hydroxy-anthraquinones is changed in alkaline solution.

—F. W. A.

**Anthradiquinones.** O. Dimroth and E. Schultze. *Annalen*, 1916, **411**, 345—350.

THE highly labile products obtained by the careful oxidation of carminic acid, kermesic acid, and laccainic acid have not yet been isolated in a pure form, but are considered to be anthradiquinones. The parent bodies of this class of substances, the 1,4,9,10- and 1,2,9,10-anthradiquinones have been prepared by the oxidation of quinizarin and alizarin respectively by means of lead dioxide and acetic acid. 1,4,9,10-Anthradiquinone is obtained as stable yellow needles (m.pt. 211°—213° C.) by precipitation from benzene solution by means of petroleum spirit; it is readily soluble in chloroform and acetone, less soluble in benzene and alcohol; the solutions are yellow without the fluorescence characteristic of quinizarin. The diquinone oxidises quinol to quinhidrone, hydriodic acid to iodine, and is rapidly reduced to quinizarin by means of sulphurous acid; quinizarin is also formed from the diquinone in aqueous solution or suspension, without addition of a reducing agent, slowly on allowing to stand and immediately on boiling, phthalic acid also being produced. On treatment with hydrochloric acid in acetic acid solution, 3-chloroquinizarin (m.pt. 239°—240° C.) is obtained. The solution of the diquinone in sulphuric acid has the bluish colour of purpurin, and not the colour of quinizarin as stated by Lesser (this J., 1915, 543); this conversion of quinizarin-quinone into purpurin is similar to the conversion of benzoquinone into hydroxyquinol discovered by Thiele. 1,2,9,10-Anthradiquinone has similar properties, but is less stable.—F. W. A.

**Quercetin from the bark of *Pinus pinaster*.** R. Lepetit and C. C. Satta. *Atti R. Accad. Lincei*, 1916, [v], **35**, i, 322—325. *J. Chem. Soc.*, 1916, **110**, i, 458—459.

THE yellow colouring matter obtained by treatment of the extract of the bark of the Tuscan pine with sodium bisulphite under pressure, and formerly regarded as fisetin (compare Lepetit, *Atti VI. Congr. Chim. Appl.*, Rome, 1905, III., 156), is now shown, by means of its dyeing properties and the constants of several of its derivatives, to consist of quercetin.

**Hydroxyazo compounds; Reactions of nitrates of** —, G. Charrier. *Gaz. Chim. Ital.*, 1916, **46**, II., 1—17.

THE author has shown previously that, under suitable conditions, nitrates of hydroxy- (or amino-) azo compounds decompose, spontaneously or on heating, to yield a nitro-hydroxy (or amino) compound and an arylidiazonium nitrate:



When the nitrates of the ethers of hydroxyazo compounds are heated with concentrated hydrohalogen acids, the arylidiazonium nitrate first formed is decomposed by the acid, furnishing chiefly the corresponding arylhalogen derivative and free nitrogen. For example the nitrate of the ethyl ether of phenylazo- $\beta$ -naphthol when heated

with hydrochloric acid, yields, in addition to the ethyl ether of nitro- $\beta$ -naphthol, chiefly chlorobenzene, but small quantities of other compounds are formed by secondary reactions. When dissolved in or heated with alcohols, the nitrates of the ethers of hydroxyazo compounds decompose in the following manner:  $\text{Ar}_1\text{N}_2\text{Ar}_2\text{OR}\cdot 2\text{HNO}_3 \rightarrow \text{Ar}_1\text{N}_2\text{Ar}_2\text{OH} + \text{R}\cdot\text{NO}_2 + \text{HNO}_3$ .—A. S.

**Anti-coagulating action of acid aniline dyestuffs on proteins.** Hollande. See XIXA.

#### PATENTS.

[*Azo dyestuff*]; *Manufacture of a green chromium compound [of an]—*. O. Imray, London. From Soc. Chem. Ind. in Basle, Switzerland. Eng. Pat. 15,064, Oct. 25, 1915.

Two different chromium compounds have been isolated from the blue solution obtained by boiling with a chromic salt the commercial *o*-hydroxyazo dyestuff (Eng. Pat. 26,460 of 1912; this J., 1913, 905) obtained by coupling in alkaline solution 4,2,1-nitrodiazophenol and 1,8-amino-naphthol-3,6-disulphonic acid (Chrome Fast Green G; Palatine Chrome Green G), viz., a sparingly soluble red compound, which gives loose reddish-violet shades destroyed by chroming, and a green compound which gives on animal fibres valuable green dyeings somewhat purer and bluer and of better fastness to light than the original dyestuff, the fastness to washing and alkali being very good and to fulling and potting satisfactory. *Example.* 47 grms. of chromium fluoride is dissolved in 1100 c.c. of hot water, 50 grms. of the commercial dyestuff (Chrome Fast Green G) added, and the liquid boiled for an hour until deep blue; 120 grms. of anhydrous sodium acetate is added, the mixture boiled for a quarter of an hour, filtered hot, and the filtrate evaporated to 500 c.c.; the red chromium compound separates and the filtrate is mixed with 150 grms. of common salt and allowed to stand until needles of the green chromium compound separate.—F. W. A.

**Colouring matters of the anthraquinone series; Manufacture of—**. J. Y. Johnson, London. From Badische Anilin und Soda Fabr., Ludwigshafen, Germany. Eng. Pat. 17,764, July 27, 1914.

SEE Ger. Pat. 287,614 of 1914; this J., 1916, 171. 4-Aminoanthraquinoneacridones may be produced by splitting off the 3-sulpho group by means of acid, alkaline, or reducing agents during or after the condensation process, or, in some cases, in the dyeing bath, or after the sulphonated compound has been applied to the fibre.

**Colouring matters of the anthraquinone series; Manufacture of— and intermediate products of such manufacture. New products of the anthraquinone series. Colouring matters of the anthraquinone series.** J. Y. Johnson, London. From Badische Anilin und Soda Fabr., Ludwigshafen, Germany. Eng. Pats. 3347, Mar. 2, 1915; 100,580, Mar. 2, 1915 (Appl. No. 2873 of 1916); and 100,581, Mar. 2, 1915 (Appl. No. 2874 of 1916).

SEE Ger. Pat. 288,464 of 1914; this J., 1916, 355. A  $\beta$ -halogenanthraquinone may be used in place of anthraquinone-2-sulphonic acid, and the resulting  $\beta$ -arylaminoanthraquinones may be condensed further with an arylamino compound other than an aminoanthraquinone, in presence of caustic alkali or alkali alkyloxide, with or without an oxidising agent. Dyestuffs of the constitution,

$\text{A} < \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{Ar}$ , where A is an anthraquinone residue, and Ar is an aryl residue other than an anthraquinone residue, are obtained. They can be used directly for the manufacture of lakes and give acid wool dyes when sulphonated. The formation of the  $\beta$ -arylaminoanthraquinones and



of the dyestuffs may be effected in one operation instead of in two stages.

*Azo dyestuffs; Manufacture of* —. Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 291,712, Nov. 28, 1914.

Azo dyestuffs are obtained from the hydrazide of 2,3-hydroxynaphthoic acid (Franzen, J. prakt. Chem., 1908, 78, 164) or its derivatives in which a hydrogen atom of the amino group is replaced by an acidyl group, by coupling them, either in substance or on the fibre, with aromatic diazo-compounds. The dyes are faster and give deeper shades than the corresponding  $\beta$ -naphthol derivatives, and are suitable for printing and for the preparation of pigments.—A. S.

*Sulphur dyestuffs; Manufacture of yellow* —. Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 292,148, Dec. 11, 1914.

PRIMARY diamines of the diphenyl series, methylated in the nucleus, or their halogen substitution products are fused at a high temperature with more than one molecular proportion of sulphur, with or without addition of benzidine; in the case of the tolidines the addition of benzidine is essential. The products dissolve readily in sodium sulphide solution and give fast, clear, greenish-yellow shades.—A. S.

*Mono- and disazo dyestuffs; Manufacture of* —. J. Hausmann, Frankfurt. Ger. Pat. 291,906, Mar. 29, 1914.

Azo dyestuffs giving shades fast to washing and to light are obtained by coupling aromatic diazo or tetrazo compounds with oxindole-6-sulphonic acid.—A. S.

*N-Dihydro-1,2,2,1'-anthraquinone-azine [Indanthrene]; Manufacture of a chlorine derivative of — fast to chlorine*. Chem. Fabr. Griesheim-Elektron. Ger. Pat. 292,127, Mar. 18, 1915.

FINELY-DIVIDED Indanthrene is suspended or dissolved in a suitable medium and treated with chlorine at about 140° C., with or without addition of a chlorine-carrier. The product may be converted into trichloroindanthrene by treatment with alkaline hydrosulphite solution. It is similar in dyeing properties to the mixture of di- and trichloro-derivatives described in Eng. Pat. 17,242 of 1905 (this J., 1905, 1298).—A. S.

## V.—FIBRES; TEXTILES; CELLULOSE; PAPER.

*Animal wools and hairs; Optical refraction of* —. A. Herzog. Chem.-Zeit., 1916, 40, 528.

THE optical properties of a series of animal fibres have been studied with the polarising microscope for purposes of comparison with results previously recorded for vegetable and artificial fibres. The mean refractive indices of the animal wool and hair fibres are fairly high, ranging from 1.549 to 1.553, as compared with 1.567 for natural silk, 1.562 for flax, 1.557 for cotton, 1.543 for cellulose artificial silks, and 1.477 for acetate silk. The differences shown by the various species of wool and hair fibres are inconsiderable, owing to the similarity of their chemical composition and microscopic structure. The differences between the refractive indices in the two main directions of the fibre, which is a measure of the specific double refraction, are only small (0.007–0.009) in the case of the wool and hair fibres, comparable in dimensions with, but opposite in sign to the value for acetate artificial silk. The differences in the case of the cellulose artificial silks are much

larger. In the case of the wools, owing to their relatively small thickness, the interference colours between crossed nicols are only low grey or whitish colours of the first order but the higher colours were studied in the case of the coarser fibres of horse-hair and pigs' bristles.—J. F. B.

*Sulphite lyes; The ammonia test for* —. E. Oman. Teknisk Tidskrift, 1916, 46, 4–6.

SULPHITE lyes as used in the manufacture of wood pulp contain about 0.9% CaO and 4% SO<sub>2</sub>. They are tested from time to time during the boiling by addition of ammonia which at the beginning produces a white precipitate of calcium sulphite; towards the end of the boiling this precipitate diminishes, and if its volume falls below a certain limit, this is generally considered as proof that too little lime has been present and the boiling is then stopped even if not finished. The author has proved that this ammonia test—also called Mitscherlich's test—as applied at present gives no indication whatever of the quantity of lime present as sulphite and is, therefore, totally useless. If sufficient sulphurous acid is present all the lime will be precipitated, including that combined with organic compounds; if not, only a very small precipitation occurs, so that the test is in reality a test for the sulphurous acid rather than for the lime. It is necessary, in using the test, to take out the samples of lye through a pipe or worm cooled by water circulation in order to prevent sulphur dioxide from escaping, but even so the test is quite illusory as a measure of the "exhaustion" of the lime. When a cooler is used, however, the Mitscherlich test may be used for estimating the amount of sulphurous acid present, provided some calcium chloride is added to the ammonia used in the test.—C. B.

*Sugar-formation in the sulphite cellulose process*. E. Oman. Teknisk Tidskrift, 1916, 46, 6–8. (See also this J., 1916, 172.)

IN most investigations of the formation of sugar during the sulphite boiling process, it has been taken for granted that the different sugars present in the lye are completely hydrolysed. The author finds that such is not always the case, and gives the results of his experiments as follows: 1. At the beginning of the boiling the lye contains a large proportion of non-hydrolysed sugar, often more of this than of hydrolysed sugar. 2. The non-hydrolysed sugar is split up by the acid liquor during the progress of the boiling, so that finally it is sometimes—but by no means always—completely hydrolysed. The hydrolysed (reducing) sugars were determined by Glassmann's method (this J., 1906, 236).—C. B.

*Paper; Partial substitution of sodium bisulphate for aluminium sulphate in the sizing of* —. B. Haas. Chem.-Zeit., 1916, 40, 571–572.

SODIUM bisulphate has been proposed as a partial substitute for aluminium sulphate in the sizing of paper, but while the impure by-product forms of the bisulphate are suitable for the sizing of the lower grades of paper, it is considered that only purified salts should be used for the finer grades. The most economical and convenient method of employing pure bisulphate is to prepare a solution, as required, by the addition of sulphuric acid to a solution of pure normal sodium sulphate, which is less costly than the pure bisulphate and keeps better on storage. In sizing the pulp, sodium bisulphate or aluminium sulphate should be added before the rosin size, in order to acidify the pulp and to inhibit the action of the saline constituents of the water and fibre upon the dilute size-milk. An equally favourable result is obtained whether the whole or only a portion of the bisulphate or aluminium sulphate solution be added before the

rosin size, but if the rosin size be added first, as is the custom in many cases, the economical effect is not realised.—J. F. B.

*Cause and nature of soil acidity with special regard to colloids and adsorption. [Acidity of washed absorbent cotton.]* Truog. See XVI.

#### PATENTS.

*Silk and similar fibres; Process for degumming* —. W. Buschhüter, Crefeld, and M. Voigt, Crefeld-Traar, Germany. Ger. Pat. 291,159, Nov. 29, 1913.

Raw silk is impregnated with a solution of an alkali salt, other than a soap, of which the acid is weaker than the amino-acids of the sericin, and is then steamed, and the sericin thus separated from the silk fibres is dissolved by means of a soap bath or by the foam from a boiling soap solution. Suitable salts are the alkali salts of silicic, boric, or stannic acid or of the acids of acaroid resin, or alkali sulphides or aluminates. With certain of these salts a bleaching and weighting action is obtained in addition.—A. S.

*Flax, hemp, and jute; Preparation of fibres from *Cyperus papyrus*, L., as a substitute for* —. P. Hoering, Berlin. Ger. Pat. 291,302, June 30, 1914. Addition to Ger. Pat. 290,605.

PAPYRUS stems before being treated with hot water as described in the chief patent (see Eng. Pat. 6971 of 1914; this J., 1915, 867), are subjected to strong pressure, either in the fresh condition or after being moistened by immersion in water. —A. S.

*Wood and other substances; Process for obtaining fibre from* —. W. K. Freeman, Oscawana, N.Y., Assignor to Hydrolase Process Corporation, New York. U.S. Pat. 1,186,655, June 13, 1916. Date of appl., Nov. 25, 1913.

THE material and chemicals are heated together in each of a series of digesters for periods insufficient to cause complete digestion in any one digester; the mass is agitated in certain of the digesters and is transferred from one digester to the next throughout the series, without cooling or exposure to the atmosphere, until digestion is complete.—J. F. B.

*Paper; Process and apparatus for reducing — to pulp.* H. Wade, London. From The General Waste-Paper Recovery Co., Baltimore, Md., U.S.A. Eng. Pat. 3702, Mar. 8, 1915.

PRINTED paper is steeped in hot water until softened, then charged into a pulping machine in the proportion of 1 part of dry paper to about 20 of water, heated to 160°—200° F. (71°—93° C.) and treated with a detergent mixture preferably containing soap, sodium silicate, and some free alkali. The pulping machine comprises a steep-walled feed hopper, a cylindrical tube closely surrounding a series of propeller blades of increasing pitch, and a delivery pipe back to the hopper. The propellers are rotated at such a high speed, e.g., 1800—2500 revs. per min., that they form cavities in the liquid surrounding them, and circulation of the contents of the machine takes place at the rate of about 1200 ft. per min. The particles of paper approaching the cavities formed by the rapidly revolving propellers are unable to take up the speed of the blades and are there subjected to an opposition of forces, one of which is due to the inertia of the paper and suspending liquid, constituting a resistance against which the propellers draw apart the component fibres. The disintegrated stock is washed in a suitable engine with a drum washer until sufficiently clean for re-manufacture into paper.—J. F. B.

*Paper and other materials; Fireproofing of* —. T. J. I. Craig, and Whipp Bros. and Tod, Ltd., Manchester. Eng. Pat. 8687, June 12, 1915. (See also Eng. Pat. 16,153 of 1914; this J., 1915, 868.)

IN the process of rendering materials non-inflammable by means of sodium aluminium carbonate, those materials in which the proofing agent cannot conveniently be precipitated *in situ*, may be treated by mixing or coating with a preparation of the double carbonate at any suitable stage in their manufacture. For instance, paper pulp may be mixed with a paste containing sodium aluminium carbonate precipitated by the action of excess of sodium bicarbonate on sodium aluminate.

—J. F. B.

*Paper; Manufacture of transparent airtight and waterproof* —. H. Oeser, Berlin-Schöneberg, Germany. Ger. Pat. 291,198, Sept. 2, 1915. Addition to Ger. Pat. 285,978 (this J., 1915, 1139).

FUSEL oil is added to the mixture of resin or wax, oil, and alcohol used for impregnating the paper, and a colouring matter or bronze powder is distributed over the surface of the impregnated paper. The fusel oil maintains the paper in a pliable condition whilst it is being manipulated and later escapes by volatilisation.—A. S.

*Paper stock screening machines.* A. R. Paull and A. E. G. Madley, Montreal, Canada. Eng. Pat. 10,808, July 26, 1915.

*Paper; Method used in the manufacture of — by machinery, together with apparatus for the purpose.* J. H. Wallin and K. Grangvist, Köpmanholmen, Sweden. U.S. Pat. 1,186,629, June 13, 1916. Date of appl., Nov. 14, 1913.

SEE Eng. Pat. 26,242 of 1913; this J., 1914, 478.

*Degumming silk; Process of* —. O. Röhm, Assignor to Röhm und Haas, Darmstadt, Germany. U.S. Pat. 1,186,440, June 6, 1916. Date of appl., Feb. 5, 1915.

SEE Eng. Pat. 2826 of 1915; this J., 1916, 418.

*Waterproofing material [for paper]; Method of healing* —. W. J. Mellersh-Jackson, London. From C. S. Bird, East Walpole, Mass., U.S.A. Eng. Pat. 18,093, Dec. 28, 1915.

SEE U.S. Pat. 1,165,367 of 1915; this J., 1916, 250.

*Gypsum product [for coating paper].* U.S. Pat. 1,178,016. See VII.

*Impregnation of leather or textile driving belts or the like.* Ger. Pat. 291,461. See XV.

#### VI.—BLEACHING; DYEING; PRINTING; FINISHING.

*Wool and silk; Effect of certain agencies upon the colour and dyeing properties of* —. M. Fort. J. Soc. Dyers and Col., 1916, 32, 184—187.

A BROWN COLOUR has been observed on wool after it has undergone any of the following treatments: exposure, heating, steaming, boiling with water, action of alkaline solutions, action of strong acids, action of certain other chemical agents; in the case of the first four agencies a prolonged treatment is required. Whenever browning occurs some modification in affinity to dyestuffs also takes place. Exposure to light for 1—2 months not only causes browning but makes the wool far more susceptible to subsequent browning under other agencies, e.g., heating, steaming, boiling, &c. Boiling with 5% sulphuric acid before exposure acts in a large degree as a preservative; the effect

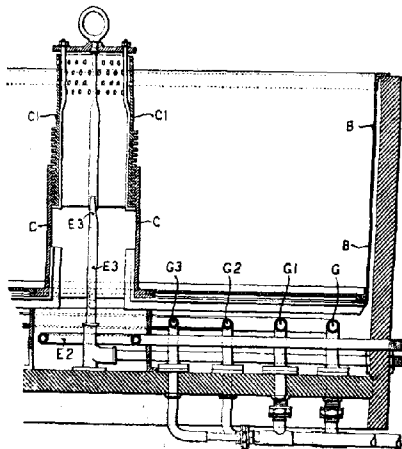
of this treatment is also preventive in the case of heating, steaming, and boiling. Stoving is no protection against the effect of exposure. Browning due to dry ironing sets in at 200° C. (after 1 minute), and definite scorching is observed at 250° C. Wool boiled with 5% sulphuric acid and stoved; wool are more resistant than ordinary wool; these treatments also improve the colour of scorched wool. The affinity for basic dyestuffs of wool browned by heat is increased, just as in the case of faded wool (see this J., 1916, 534). The influence of steaming on the affinity for dyestuffs has already been noted (*loc. cit.*), also the reversibility of the effects when the treatment is prolonged. The browning of wool under the action of steaming is progressive with the duration of treatment. Previous treatment with sulphuric acid prevents the browning and a subsequent treatment is largely curative; stoving is still more effective in restoring the colour of steamed wool. Wool after being boiled with water readily turns brown on subsequent exposure; treatment with sulphuric acid acts favourably. Boiling with organic acids followed by repeated extraction with boiling water gives a product very liable to turn brown on keeping. Wool thus browned shows an increased affinity for basic, acid, and cotton dyestuffs. The action of dilute alkalis is well known; browning is progressive and fibre substance is dissolved. Previous acid treatment and stoving are protective only until the combination of fibre and acid has been decomposed by the alkali. Immersion in cold strong acids, even in a saturated solution of sulphurous acid, develops a brown coloration of wool, which however disappears on dilution. The browning of wool by exposure, heating, steaming, and boiling would appear to be connected with the development and degradation of amino-acids; oxidation by the action of the air also plays a secondary part, as is shown by the difference between heating in an atmosphere of inert gas and in air. Silk is a much less basic fibre than wool and is less susceptible to the browning agencies; at the same time sulphuric acid has a less effective protecting influence.

—J. F. B.

#### PATENTS.

*Dyeing, etc., textile materials; Apparatus for* — A. J. Craig, Galashiels, N.B. Eng. Pat. 9372, June 26, 1915.

The direction of circulation of the dye-liquor, etc.,



is reversed without violent agitation of the liquid, by use of steam passing through the perforated

ring, E<sup>2</sup>, or the nozzle, E<sup>3</sup>, in which case the liquor ascends the telescopic pipe, C, and passes through the perforations in C<sup>1</sup>, or alternatively by use of the steam coils, G, G<sup>1</sup>, etc., in which case the liquor passes directly up into the cage, B, containing the material to be treated. In dyeing wool, uniform results are obtained and the wool is not felted.—F. W. A.

*Dyeing yarn [with vat dyestuffs]; Process of* — A. Schlegel, Mannheim, Assignor to Badische Anilin und Soda Fabr., Ludwigshafen, Germany. U.S. Pat. 1,185,943, June 6, 1916. Date of appl., Nov. 3, 1911.

SEE Addition of Mar. 7, 1911 to Fr. Pat. 359,466 of 1905; this J., 1911, 1052. The process is applicable to anthracene vat dyes in general.

*Dyeing artificial leather; Process for* — R. Weeber, Bärn, Austria-Hungary. U.S. Pat. 1,186,052, June 6, 1916. Date of appl., June 24, 1914.

THE fabric is first impregnated with a mixture of cellulose esters and a suitable mordant, and afterwards dyed with basic dyestuffs.—F. C. T.

*Aniline Black; Production of* — A. Ehrenzweig, Charlottenburg. Ger. Pat. 291,955, Dec. 9, 1913.

ANILINE Black is produced by the interaction, at a high temperature, of aniline, a diamine, and chloric acid, with or without another oxygen-containing mineral acid, but without a salt of copper, iron, manganese, vanadium, or chromium. The dye-bath is stable and can be centrifuged without alteration, so that it is applicable to the machine dyeing of tissues, yarn, cops, etc. of cotton and of union goods (half-wool and half-silk). The black is very fast and is not affected by sulphur dioxide, and the method is particularly suitable in cases where resist-discharges are to be produced by Prud'homme's method.—A. S.

*Black shades on wool; Production of* — Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 291,021, May 2, 1914.

Wool is dyed a deep black, fast to milling and to light, by treatment in a solution of a mono- or polysulphonic acid of a *p*-amino- or *p*-arylamino-aryl-*β*-naphthylamine or a substitution product and then oxidising, either in the same or a separate bath, by means of a chromate, bichromate, or chromic acid, with or without addition of acids or salts.—A. S.

*Fast [khaki] shades on wool; Production of* — Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 291,456, Apr. 26, 1914.

LEVEL khaki shades, fast to washing, milling, and rubbing, and very fast to light, are obtained by dyeing wool in baths containing dihydroxy- or aminohydroxynaphthalenesulphonic acids and copper salts, with or without addition of other salts or oxidising agents.—A. S.

*Dyeing dead or living hairs, furs, feathers, or the like* — F. Fresenius and A. Zimmer, Frankfurt. Ger. Pat. 291,133, Dec. 22, 1914.

FAST shades are produced by dyeing with aromatic hydroxy or amino compounds, with addition of salts of nickel, cobalt, manganese, bismuth, iron, or the like.—A. S.

*Laundrying and cleaning; Souring agent for — and process of using the same* — W. F. Elwood, Greensburg, Pa. U.S. Pat. 1,186,300, June 6, 1916. Date of appl., Dec. 7, 1915.

FABRICS showing stains are treated with a solution of an acid sulphate salt or other soluble oxygen compound of sulphur having an acid reaction, and a "stabiliser," e.g., sodium silicate.—J. F. B.

*Bleaching fabrics in open form; Process of*——. C. Taylor, North Adams, Mass., U.S.A. Eng. Pat. 15,733, Nov. 8, 1915. Under Int., Conv., Nov. 11, 1914.

SEE U.S. Pat. 1,146,461 of 1915; this J., 1915, 901.

*Manufacture of azo dyestuffs.* Ger. Pat. 291,712. See IV.

## VII.—ACIDS; ALKALIS; SALTS; NON-METALLIC ELEMENTS.

*Sulphuric acid-water mixtures; The properties of mixed liquids. I. [Surface tension of]*——. J. L. R. Morgan and C. E. Davis. J. Amer. Chem. Soc., 1916, 38, 555–568.

THE surface tensions of mixtures of sulphuric acid and water were determined at various temperatures, and formulæ are given for calculating the surface tension and specific cohesion at any concentration and at any temperature between 0° and 50° C. The surface tension was measured by determining the weight of a falling drop (Morgan, J. Amer. Chem. Soc., 1915, 37, 1461), and a mode of applying the method to liquids of high viscosity is described. Both the addition of sulphuric acid to water and of water to sulphuric acid causes an increase in the surface tension, so that different concentrations of sulphuric acid may have the same surface tension at the same temperature. The addition of sulphur trioxide to sulphuric acid also increases the surface tension. The results obtained and the variation of other physical properties with concentration are discussed in their bearing on the question of hydrate formation in mixtures of sulphuric acid and water.

—F. SODN.

*Selenic acid; Reduction of*——. W. O. de Coninck and Chauvenet. Ana. Chim. Analyt., 1916, 21, 114.

WHEN a mixture of formic acid with a slight excess of colourless selenic acid (sp.gr. 1.4) is heated gradually to boiling, carbon dioxide is disengaged and selenium is precipitated. Malonic and pyruvic acids also reduce selenic acid: acetic and succinic acids do not; boiling with oxalic acid causes only partial reduction. The selenium deposited has a dark reddish-brown colour, is amorphous, and practically insoluble in carbon bisulphide; it is apparently identical with that obtained by reducing selenic acid with sulphur dioxide.

—E. H. T.

*Carbonic acid; The time reaction in the neutralisation of*—— and the true dissociation constant of carbonic acid. L. Pusch. Z. Elektrochem., 1916, 22, 206–212.

THE reaction  $\text{OH}' + \text{CO}_2 \rightarrow \text{HCO}_3'$  is the determining factor of the reaction velocity of the neutralisation of carbonic acid. Measurements with the pure acid showed that no alteration of conductivity with the time occurred, hence the above reaction is apparently so accelerated by the hydrogen ions that the time reaction is no longer measurable. A similar catalytic action of hydrogen ions occurs in the conversion of  $\gamma$ -hydroxy fatty acids into lactones. In the neutralisation of carbonic acid the reaction velocity is proportional to the concentration of the acid and base and inversely proportional to that of the bicarbonate. The mean value at 0° C. is  $k = 0.043$ . By means of the "residual current" the concentration of the undissociated molecule  $\text{H}_2\text{CO}_3$  was determined, whence the dissociation constant  $k = \frac{[\text{H}][\text{HCO}_3]}{[\text{H}_2\text{CO}_3]}$  was found to be  $7.42 \times 10^{-4}$ , a value which is greater than that of acetic acid.—G. F. M.

*Ammonia; Synthesis of*——. C. Zenghelis. Comptes rend., 1916, 162, 914–916.

VARYING small yields of ammonia were obtained by passing mixtures of nitrogen (1 vol.) and hydrogen (3 vols.) through water at 90° C., in the presence of a colloidal or finely divided metal as catalyst. The metals used were platinum, palladium, silver, copper, mercury, and gold, and in most cases the yields were considerably increased, although still small, by acidulating the water. Colloidal silver, prepared by Carey Lea's method, was most effective. Ammonia was also produced in small quantities by passing nitrogen through a mixture of zinc and dilute sulphuric acid, at 90° C., or into contact with nascent electrolytic hydrogen, also by passing hydrogen through a warm solution containing ammonium chloride and sodium nitrite; but a much larger yield was obtained by the last method in presence of a metallic catalyst, and, in this way, using colloidal palladium, as much as 40% of the nitrogen present was converted into ammonia.—F. SODN.

*Soda-lime; Properties of*——. I, II, and III. I. Guareschi. Atti. R. Accad. Sci. Torino, 1916, 51, 4–26, 59–82, and 263–278. J. Chem. Soc., 1916, 110, ii., 324–325.

MANY reactions which do not take place with sodium or potassium hydroxide or lime, or take place only at high temperatures, occur at the ordinary temperature, and sometimes violently when soda-lime is employed. Further, soda-lime constitutes the most efficient agent to combat poisonous, irritating, or tear-producing gases, since it readily absorbs chlorine, bromine, halogen hydrides, carbon dioxide, sulphur dioxide, carbonyl chloride, cyanogen, hydrogen cyanide, cyanogen chloride, bromide and iodide, sulphur chloride, thionyl chloride, nitrosyl chloride, nitrogen peroxide, hydrogen arsenide, antimonide, sulphide, and selenide, mercaptans, thiocyanic acid, indole, scatole, aldehydes, chlorocarbonic esters, aromatic chloro- and bromo-derivatives with the halogen in the side-chain, ethyl bromoacetate and chloro-acetoacetate, chloroacetone, bromoacetophenone, acetic anhydride, etc. The soda-lime acts far more energetically when recently prepared and stored in a hermetically sealed vessel. 100 grms. of soda-lime in fine granules will absorb 1500–2250 c.c. of carbonyl chloride. Hydrogen sulphide is readily absorbed by soda-lime, and the reaction is attended with the development of a very considerable amount of heat; when the current of gas is mixed with air the soda-lime becomes incandescent, whilst replacement of the air by oxygen results in a violent explosion. This incandescence is observed only with freshly-prepared soda-lime, which should consist of granules 1–3 mm. in diameter. 100 grms. of soda-lime absorbs 35 litres of hydrogen sulphide. Soda-lime also absorbs hydrogen selenide, which produces rapid and intense irritation of the mucous membrane of the nose and is capable of paralysing the sense of smell for some hours or even days. Sulphur dioxide is absorbed by soda-lime, rapidly at first and subsequently more slowly, 26 litres being taken up by 100 grms. The mixture of hydrogen chloride, nitrosyl and nitroxyl chlorides, and chlorine obtained from *aqua regia* is also rapidly absorbed, and the same is the case at first with cyanogen, of which more than 6 litres is absorbed per 100 grms.; the employment of soda-lime to retain the cyanogen emitted from blast-furnaces is suggested. Carbon monoxide at the ordinary temperature is absorbed but slightly or not at all. In presence of soda-lime, ammonia causes at the ordinary temperature reactions which otherwise occur only at high temperatures. Hydrogen phosphide, prepared by passing hydrogen into a flask containing 45

—50% potassium hydroxide solution, and a few pieces of phosphorus, is spontaneously inflammable, but loses this property when passed through soda-lime; the latter also absorbs phosphorus vapour. Soda-lime may be used to purify the hydrogen obtained by the action of acid on iron or zinc, but it will not remove hydrogen phosphide, which is detected by the green colour of the flame. Soda-lime absorbs many of the impurities of coal-gas and takes away its foetid odour; similar purification and deodorisation occur with acetylene, which is not absorbed by soda-lime.

*Alkaline earths with alkali hydroxides; Mixtures of the —.* I. I. Guareschi. Atti R. Accad. Sci. Torino, 1916, 51, 372—377. J. Chem. Soc., 1916, 110, ii., 325.

THE incandescence observed when a mixture of air and hydrogen sulphide is passed over soda-lime (preceding abstract) also occurs when the latter is replaced by a mixture of lime or, better, baryta with sodium or potassium hydroxide, even when the latter is present in relatively small proportion; potassium hydroxide is more effective than sodium hydroxide. A negative result is obtained when the lime or baryta is replaced by glucinum oxide.

*Apatites; Composition of —.* F. Zambonini. Comptes rend., 1916, 162, 919—921.

CRYSTALS having the formula,  $\text{CaCl}_2 \cdot 4 \cdot 34 \text{Ca}_3(\text{PO}_4)_2$ , were obtained by fusing tricalcium phosphate with sodium chloride and washing the product with water. The crystals were more highly birefractive than ordinary chlorapatite,  $\text{CaCl}_2 \cdot 3 \text{Ca}_3(\text{PO}_4)_2$ , and are regarded as a solid solution of this double salt with calcium phosphate. —F. SODN.

*Palladous salts; Catalytic action of — in oxidation reactions.* G. Scagliarini and G. B. Berti-Ceroni. Gaz. Chim. Ital., 1916, 46, II., 51—56.

PALLADOUS salts accelerate the oxidation of oxalic acid and of ammonia by persulphates and, in a lesser degree, the oxidation of oxalic acid by nitric acid. The effect is due to the action of the palladous salt as an oxygen-carrier. It is oxidised by nitric acid and, more readily, by persulphates to a palladic compound, which in turn is decomposed by oxalic acid or by ammonia. —A. S.

*Tetrathionates in alkaline solution; Decomposition of — as a source of error in certain iodine titrations.* R. M. Chapin. J. Amer. Chem. Soc., 1916, 38, 625—626.

TETRATHIONATES are affected only slightly by sodium bicarbonate and still less by sodium bicarbonate in the presence of carbonic acid, but are sensitive to hydroxyl ions even in low concentration. The treatment of solutions containing tetrathionates with distinctly alkaline substances, before titrating with iodine (this J., 1914, 481), should therefore be avoided, and in the determination of arsenic by Williamson's method (this J., 1896, 474) or its modifications, it is preferred to use a dilute solution of sodium sulphite (containing about 0.5% of the anhydrous salt), instead of thiosulphate, as a discharging agent for the liberated iodine. —F. SODN.

*CaO-Al<sub>2</sub>O<sub>3</sub>-MgO; The ternary system —.* G. A. Rankin and H. E. Merwin. J. Amer. Chem. Soc., 1916, 38, 568—588.

AN investigation of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$  by the method of thermal analysis involved equilibrium of the three components themselves and the binary compounds  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ , and  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  in ternary solutions, no ternary compounds being

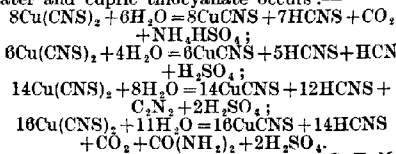
stable in contact with the melts. Equilibrium relations are exhibited in a series of tables and diagrams and in a representation of the concentration-temperature solid model; these show 8 fields of stability, 13 boundary curves, and 6 quintuple points, two of which are eutectic points. The same types of ternary crystallisation are found as in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (this J., 1915, 139), and an equilibrium diagram is given which serves to indicate, when the original composition of a ternary melt is known, the composition of the solid phases which will crystallise from it on slow cooling, the order in which the phases will separate, and the final product of crystallisation. In addition to the properties of the components and binary compounds previously given (this J., 1909, 1124), further observations have been made on the optical characters of the compounds  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , and a new ( $\beta$ ) form of alumina, which occurred occasionally in charges of pure alumina, after melting and slow cooling, and which appears to be monotropic with respect to the  $\alpha$  form (corundum), is described. The compound  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  (*loc. cit.*) melts at  $2135^\circ \text{C} \pm 20^\circ$  and forms eutectics with magnesium oxide and also with both forms of alumina. —F. SODN.

*Aluminium nitrate; Hydrates of —.* R. Seligman and P. Williams. Chem. Soc. Trans., 1916, 109, 612—617.

ALUMINIUM nitrate crystallises in at least three forms each of which is stable in nitric acid of specific strengths. A hydrate  $\text{Al}(\text{NO}_3)_3 \cdot 18 \text{H}_2\text{O}$  is deposited in small needles from nitric acid solution of sp. gr. 1.42. It is the least soluble and most stable hydrate at  $20^\circ \text{C}$ . in nitric acid of this strength. In nitric acid of sp. gr. 1.5 the hydrate  $\text{Al}(\text{NO}_3)_3 \cdot 12 \text{H}_2\text{O}$  is alone stable, and is moreover deposited initially from solutions of aluminium in the above mentioned weaker acid in large lozenge-shaped crystals which change spontaneously into the octodecahydrate. In acids of intermediate strength a hydrate containing 15 or 16  $\text{H}_2\text{O}$  and crystallising in thin plates, is the stable form. —G. F. M.

*Cupric thiocyanate; Action of water on —.* J. C. Philip and A. Bramley. Chem. Soc. Trans., 1916, 109, 597—603.

CUPRIC thiocyanate, precipitated from cupric chloride solution by excess of potassium thiocyanate, is slowly acted on by the water present, reduction to cuprous thiocyanate being ultimately complete. The other products formed concurrently, namely, carbon dioxide, ammonia, urea, hydrogen cyanide, and thiocyanic and sulphuric acids, were found to account quantitatively for the oxidised thiocyanogen radicle. When cupric thiocyanate was precipitated from cupric acetate solution cyanogen was formed in addition to the substances already specified. The following equations are suggested as representing the different ways in which the reaction between water and cupric thiocyanate occurs:—



—G. F. M.

*Manganic compounds; Constitution of —.* J. Meyer. Z. Elektrochem., 1916, 22, 201—202.

THE colour of manganic salts depends largely on external circumstances, and in all cases the absorption spectra are practically identical, hence

the conclusion of Sem (this J., 1915, 1248) that there are two series of manganic salts is unwarranted. The existence of manganic nitrate is extremely doubtful, the solution obtained by Sem being in all probability a colloidal hydrated manganese dioxide. In pure manganic chloride solutions no manganous ions are present, hence Sem's views on the existence of di- and quadri-valent manganese in equilibrium with trivalent ions are incorrect.—G. F. M.

*Radium; Experiments on the extraction of— from carnotite ores with concentrated sulphuric acid.* H. Schlundt. J. Phys. Chem., 1916, 20, 485—494. (See also U.S. Pat. 1,181,411 of 1916; this J., 1916, 690.)

THE carnotite ores of Colorado and Utah consist of a sandstone with a clay binder which carries the mineral carnotite, a hydrated potassium uranium vanadate containing some barium and calcium. The experiments were conducted on a low-grade ore containing 1.66% of uranium (as  $U_3O_8$ ), 4.03% of vanadium (as  $VO_2$ ), 1.36% of moisture, and 4.88 parts per billion of radium; also on a high-grade ore with 14.39% of uranium, 9.67% of vanadium, and 42.78 parts per billion of radium. Experiments with 100 gm. charges of the former showed that treatment with 78% (60° R.), or stronger, sulphuric acid gave a radium extraction of fully 90%, and that the vanadium and uranium were completely removed with 35% acid. Temperature conditions were of less moment than concentration of acid. At the ordinary temperature 90% acid gave an extraction of 84% from the low-grade ore in 24 hours, but 15 minutes sufficed when the charge was added to boiling 78% acid and was well stirred in. The high-grade ore was less easily extracted; one hour's treatment with 90% acid up to 290° C. removed 89% of the radium. Large-scale experiments were conducted with 10 kilo. charges of ore ground to pass through a 20-mesh sieve. The charge was introduced gradually into 18 litres of 78% acid at 190° C. contained in a 50-litre cast iron vessel, and heated to 220° C. for at least 15 mins. Uranium, vanadium, and some iron and aluminium are thus converted into soluble compounds and the calcium, barium, and radium are dissolved as bisulphates. The liquid is cooled to 130° C., and the insoluble silicates and silica are filtered off on a stoneware filter packed with "Filtros" under a pressure of 5–10 cm. of mercury, the coarser particles being poured in first. The residue is dry within 30 mins. and is then washed with two successive portions of 5 litres of the hot concentrated acid. The acid filtrate is poured into eight times its bulk of hot water, whereby the radium and barium sulphates are precipitated, and by adding dilute barium chloride solution (5 grms. per 100 litres) a 2% increased extraction of radium is obtained. After standing for at least 3 days the supernatant liquid is siphoned off, and the crude sulphates are washed on a filter with hot water containing a trace of barium chloride, and then dried. With low-grade ore, radioactivity measurements of these sulphates show that the radium concentration is 235 times greater than that of the original charge; with high-grade ore it is only 35 times greater. The residue on the suction filter contains soluble vanadium, uranium, and iron sulphates, together with acid retaining some radium. By washing it several times with hot water and stirring thoroughly (on the filter), a deep blue filtrate is obtained which gradually deposits a white precipitate containing 3–9% of the original radium content of the ore. The actual recovery of radium was slightly less than was expected from the estimate of the losses in tailings and solutions.—E. H. T.

*Inorganic hydrogels; Effect of freezing on certain —.* [Hydrogels of alumina, silica, and ferric oxide.] H. W. Foote and B. Saxton. J. Amer. Chem. Soc., 1916, 38, 588—609.

HYDROGELS of alumina, silica, and ferric oxide, containing known proportions of total water, were subjected to progressive cooling in a dilatometer, as long as the influence of freezing was apparent on the volume-temperature curve. After removal of all water present in its usual free condition, the volume continued to increase somewhat down to a low temperature (below—20° C.), owing, it is thought, to the freezing of adsorbed or capillary water, of lower vapour pressure and therefore lower freezing point than "free" water. The proportions of free and capillary water were calculated from the expansion effect, whilst the difference between their sum and the total water is taken as combined water. The capillary and combined water correspond to that previously supposed to be in solid solution (Poote, J. Amer. Chem. Soc., 1908, 30, 1388); but the free water, determined by the dilatometer method, includes part of the capillary water, on account of supercooling, so that the "apparent capillary water" given (that separating below —6° C.) is too low. With aluminium hydroxide, the amount of capillary water did not change when the free water was allowed to evaporate; but repeated freezing, whilst having little effect on the combined water, converted most of the capillary water into free water; after standing for 8 months, however, the total free and capillary water had increased at the expense of the apparently combined water, and with such material (considered as best representing equilibrium), 37.1% of combined water was obtained, as against 34.6% calculated for the formula  $Al(OH)_3$ . Silicic acid contained a much higher proportion of capillary water than aluminium hydroxide (over 0.7 gm. per gm.  $SiO_2$ ), and the proportions of free and capillary water were but little altered by successive freezings; the percentage of combined water corresponded approximately to the formula  $SiO_2 \cdot 1.3H_2O$ . With ferric hydroxide, freezing caused very little change in the capillary water, but from the form of the volume-temperature curves, this water is thought to be more firmly held or lodged in finer capillaries than in the other colloids examined; the proportion of combined water corresponded to the empirical formula  $Fe_2O_3 \cdot 4.25H_2O$ .—F. SODN

*Cobaltous oxide and other metallic oxides; Reactions between — at high temperatures.* J. A. Hedvall. Z. anorg. Chem., 1915, 93, 313. Chem.-Zeit., 1916, 40, Rep., 196. (See also this J., 1915, 1052.)

RINMAN'S green probably does not consist of zinc oxide and cobaltous oxide, but of cobalt-zincate and zinc oxide. The crystals are not isodimorphous, but hexagonal structures of hexagonal white zinc oxide and hexagonal green cobalt-zincate. The green colour could not be produced additively from brownish prismatic cobalt oxide and zinc oxide. Cobaltous oxide gives with glucinum (beryllium) oxide only a dark grey mass; with chromic oxide a green octahedral spinel,  $CoO \cdot Cr_2O_3$ ; and with titanium oxide a metatitanate,  $CoO \cdot TiO_2$ . No compounds are formed with zirconium oxide, thallium oxide, cerium oxide, or silica, but crystalline vanadates and tantalates are formed.—T. ST.

*Nitrogen; An active modification of —.* VII. R. J. Strutt. Proc. Roy. Soc., 1916, A, 92, 438—450. (See also this J., 1915, 422.)

THE production of active nitrogen from a steady discharge obtained from a direct current dynamo, using a tube 18 mm. diameter, between aluminium disc electrodes 130 mm. apart, is greatest near the

cathode, falls off to a minimum in the Faraday dark space, and increases again in the positive column to a value constant along that column but less than at the cathode. A much greater yield of active nitrogen is obtained from the positive column in a narrow tube of 6 mm. diameter than in a wide one of 15 mm. diameter. The potential gradients in the wide and narrow tubes were nearly the same in each case, so that the different yields of active nitrogen cannot be attributed to the potential gradient, but must rather be connected with current density. As the length of positive column traversed by the gas is increased, the yield of active nitrogen increases to a limit, owing to a destructive action of the discharge which beyond a certain concentration destroys the active nitrogen as fast as it is produced. It is known that a trace of oxygen, or other gas, increases the yield of active nitrogen, and the amount of oxygen required considerably increases the fall of potential at the cathode, but it does not measurably affect the fall of potential in the positive column. A smaller quantity of active nitrogen is produced at atmospheric pressure than at the usual pressure of 5 mm. of mercury or less, owing to the destructive action of the surrounding gas on the active nitrogen as it is produced. If a copper cathode be employed the metal disintegrated by the discharge emits its line spectrum excited by active nitrogen, as in those cases where active nitrogen is led over a heated metal.—W.G.C.

*Oxygen; Solubility of*—in salt solutions, and the hydrates of these salts. C. G. MacArthur. J. Phys. Chem., 1916, 20, 495–502.

THE solubility of oxygen in aqueous solutions of various concentrations of the following substances was determined by Winkler's manganous hydroxide method: the chlorides of lithium, sodium, potassium, rubidium, caesium, ammonium, magnesium, calcium, barium; the bromides and sulphates of sodium and potassium; the iodide and nitrate of potassium; and sucrose. In every case the solubility diminished regularly with increasing salt concentration, and with ammonium chloride the diminution was particularly great. The values obtained for the solubility in sucrose solutions were low and somewhat unreliable owing to the sugar being slowly oxidised by the dissolved gas.—E. H. T.

*Phosphorus; The system*—from the point of view of the theory of allotropy. A. Smits and S. C. Bokhorst. Z. physik. Chem., 1916, 91, 249–312. J. Chem. Soc., 1916, 110, ii., 317–319.

THE vapour-pressure curves of molten white and violet phosphorus were found to belong to one and the same vapour-pressure curve, indicating that liquid white phosphorus may be termed supercooled liquid violet phosphorus. When violet phosphorus has not been completely freed from white phosphorus by extraction with carbon bisulphide, the vapour pressure is always too high. Above 450° C. the last traces of white phosphorus are transformed with measurable velocity into violet phosphorus, and the vapour pressure sinks to the value appropriate for the violet phosphorus. Red phosphorus is a metastable modification, which never exists in internal equilibrium and is not a homogeneous substance. The authors term it "red-coloured phosphorus," and characterise it as a mixture of mixed crystals of varying composition. The only stable solid modification of phosphorus is violet phosphorus (the metallic phosphorus of Hittorf), and the colour of this depends on the size of the particles, as is shown by the fact that, using the same method of preparation, red specimens and violet specimens are obtained which have the same vapour pressure and specific gravity. Graphically it has been shown that the triple

point of violet phosphorus lies at 589.5° C. and 43.1 atms. An exact experimental determination gives 589.5° C. as the temperature of the triple point. The heat of sublimation,  $Q_{sg}$ , has the very high value of 25.839 Cal.; it is not a function of the temperature. The heat of fusion  $Q_{sl}$ , is 15.618 Cal. A particular confirmation of the theory of allotropy is furnished by the fact that when violet phosphorus is rapidly and partly vaporised in a vacuum at a temperature where the internal equilibrium is only slowly set up, a substance of abnormally low vapour pressure is obtained. This experiment proves that the more volatile component has been expelled at a temperature at which it can only slowly be re-formed. The vapour pressure of this substance increases continuously at constant temperature, and after the addition of 0.1% of iodine and heating at 410° C. the internal equilibrium is again set up and the vapour pressure becomes normal.

*Phosphorus; Black*—P. W. Bridgman. J. Amer. Chem. Soc., 1916, 38, 609–612.

ATTEMPTS to prepare black phosphorus (this J., 1914, 787), by heating the violet and bright red varieties of red phosphorus, alone and with iodine or metallic sodium as catalyst, at 200° C. under pressure, were unsuccessful, but, in the presence of iodine, bright red phosphorus was converted into violet phosphorus. Black phosphorus is stable, compared with white phosphorus, at 200° C. at pressures above 4000 kilos. per sq. cm., and probably at lower pressures; violet is stable, compared with white phosphorus, somewhat below 200° C. at 4000 kilos.; and violet phosphorus is stable, compared with red phosphorus, at 200° C. under 8000–12,000 kilos. pressure. Sodium acted as a very efficient catalyst in converting white phosphorus into the violet modification.—F. SODN.

*Graphite; Purification of*—, particularly from sulphur and iron. E. Donath. Chem.-Zeit., 1916, 40, 579.

THE graphite is either heated with zinc dust, air being excluded, or treated with permanganate in presence of caustic soda. In either case the product is treated with hot hydrochloric acid and washed with water.—G.F.M.

*Hydrogen peroxide as hydrolytic agent.* Dubsky. See III.

*Potassium chlorate and perchlorate as substitutes for nitre in the glass industry.* Springer. See VIII.

*Recovery of ammonium molybdate from filtrates in the determination of phosphorus in iron and steel.* Friedrich. See X.

*Pickling steel with sodium bisulphate.* Le Chatelier and Bogitch. See X.

*Action of carbon dioxide on some metals and metallic compounds.* Von Bacho. See X.

*Chemical and physical properties of artificial zeolites.* Von Sigmund. See XVI.

*Ninhydrin reaction with amino-acids and ammonium salts.* Harding and Warneford. See XX.

*Separation of thorium from iron with the aid of cupferron.* Thornton. See XXIII.

#### PATENTS.

*Nitre cake; Recovery of sulphuric acid from*—J. Mackenzie, Middlesbrough. Eng. Pat. 13,907, Sept. 30, 1915.

NITRE cake is melted in the pot of an ordinary

salt-cake furnace, and when the moisture and weak acid have been eliminated, the charge is pushed on to the roaster, and the sulphuric acid expelled and led into a Glover tower or other suitable apparatus.—W. G. C.

*Sulphuric acid residues [from petroleum refining]; Process for the treatment of —.* J. S. and A. A. Blowski, Oakland, Cal. U.S. Pat. 1,186,373, June 6, 1916. Date of appl., Jan. 30, 1915.

WASTE acid from petroleum refining is separated from tarry matter by dilution with water, and the diluted acid is rapidly distilled in order to minimise the reduction of sulphuric acid by organic matter present, and to obtain a distillate with a maximum amount of hydrated sulphuric acid.—E. H. T.

*Antimonates [for clouding glass and enamels]; Manufacture of —.* P. Eyer, Halberstadt, Germany. Eng. Pat. 11,083, July 30, 1915. Under Int. Conv., Aug. 5, 1914.

VERY pure antimonates, of white colour and voluminous structure, are prepared by heating oxides of antimony with one or more bases to a high temperature in presence of ammonium nitrate. The latter is volatilised during the reaction. Antimonates made in this way, particularly those of magnesium and zinc, are especially valuable for clouding glasses and enamels; for this purpose an excess of bases should be used.—E. H. T.

*Electrolysis and treatment of [cadmium or copper] sulphate liquors.* E. J. Hunt, Oldbury, and W. T. Gidden, Warley, Worcestershire. Eng. Pat. 14,273, Oct. 8, 1915. Addition to Eng. Pat. 11,634, May 19, 1913 (this J., 1914, 692).

THE process claimed in the main patent, is applied to solutions of cadmium and copper sulphates, and the anode mud produced in the process, e.g., lead or manganese peroxide, is used for separating impurities of iron from the solutions before electrolysis.—B. N.

*Sodium perborate; Manufacture of —.* Deutsche Gold- u. Silber-Scheide-Anstalt vorm. Roessler, Frankfurt, Germany. Eng. Pat. 14,292, Oct. 8, 1915. Under Int. Conv., Oct. 26, 1914.

GRANULATED borax is suspended in a solution of alkali carbonate which is electrolysed, the electrolysis being continued until all the borax is transformed into crystallised sodium perborate. Some impurities in the electrolyte known to be catalysers, such as iron compounds, retard the formation of sodium perborate; these can be removed or their harmful effect destroyed by the addition of negative catalysers exerting a protective action, such as stannic acid, sodium perborate, or sodium bicarbonate.—W. G. C.

*Potassium chloride; Process for obtaining — from certain waters.* N. Wrinkle, Keeler, and W. W. Watterson, Bishop, Cal. U.S. Pat. 1,184,806, May 30, 1916. Date of appl., Dec. 15, 1915.

WATERS containing sodium chloride, sulphate, and carbonate in addition to potassium chloride are first treated with carbon dioxide gas in order to produce an amount of sodium bicarbonates sufficient to form "urao" ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) with the unaltered carbonate. The solution is then concentrated by evaporation, and the urao which separates is removed; by concentrating the solution further, sodium chloride and sulphate separate, and finally the potassium chloride is obtained from the mother-liquor by cooling and crystallisation.—J. B. C. K.

*Potassium chloride; Process for cooling and drying hot residues from the manufacture of —.* O. Bothner, Leipzig. Ger. Pat. 291,793, Mar. 25, 1914.

THE residues left after the extraction of potassium chloride from potash minerals are cooled and dried by transporting them pneumatically through pipes.—A. S.

*Titanic oxide concentrate and method of obtaining the same.* A. J. Rossi and L. E. Barton, Niagara Falls, Assignors to Titanium Alloy Manufacturing Co., New York. U.S. Pat. 1,171,542, Feb. 15, 1916. Date of appl., May 22, 1914.

A TITANIC oxide concentrate readily soluble in concentrated sulphuric and other acids, is obtained by fusing the ore, e.g., ilmenite, in an electric or reverberatory furnace, with a reducing agent, preferably petroleum coke, and an alkali sulphate or bisulphate, such as nitre-cake or salt-cake. The proportion of the latter must be such that the iron in the ore is converted into sulphide, the titanium into alkali titanate, and the silica and alumina into alkali silicates and aluminates: sufficient carbon must be used to ensure the reduction of the sulphate to sulphide. The solidified melt will disintegrate to a fine powder on exposure to the air for one or two days, or it may be crushed at once. It is then boiled with dilute sulphuric acid (in an amount slightly in excess of that required to combine with the bases present), whereby the iron, silicates, aluminates, etc., remain in solution, but not the titanium oxide which after separation and drying is left as a light or dark grey powder, containing from 65%–80% of the oxide, sodium, free sulphur, sulphate, and smaller amounts of silica, iron oxide, carbon and combined water. When calcined it turns yellow, and its titanic oxide content is raised about 2%.—E. H. T.

*Gypsum product [for coating paper].* W. Hoskins, Chicago, Assignor to Best Brothers Keene's Cement-Co., Medicine Lodge, Kans. U.S. Pat. 1,178,016, Apr. 4, 1916. Date of appl., Nov. 29, 1915.

NATURAL gypsum is crushed and after mixing with water is ground in a ball mill to a degree of fineness considerably greater than that of the red corpuscles of the blood. The ground product is then separated and collected by flotation and is an exceedingly fine, velvety, uniform and amorphous powder, equal or superior to china-clay as a coating for paper.—W. G. C.

*Ammonium sulphate; Manufacture of — from magnesium sulphate and ammonia.* H. Precht, Hanover. Ger. Pat. 292,218, May 4, 1915.

MAGNESIUM sulphate solution is treated with excess of ammonia, preferably under pressure, and the resulting solution is concentrated, the excess of ammonia being recovered. Ammonium-magnesium sulphate crystallises out first, leaving nearly pure ammonium sulphate in solution. The ammonium-magnesium sulphate may be treated with a further quantity of ammonia to convert it into ammonium sulphate and magnesium hydroxide.—A. S.

*Sulphur wells; Operating —.* W. D. Huff, La Fayette, La., Assignor to L. G. Moss, New Iberia, La. U.S. Pat. 1,184,649, May 23, 1916. Date of appl., July 8, 1915.

A WELL-CASING closed at the top is provided with perforations near the bottom, and also with one or more electric heaters mounted near the perforated portion of the casing. Water supplied to the casing is heated by the heaters and passes through the perforations into the sulphur-bearing strata. The molten sulphur is raised to the surface through



an inner pipe which passes down and projects beyond the bottom of the casing.—J. B. C. K.

*Basic ferric sulphate liquor; Process of forming* —. S. S. Sadtler, Montgomery County, Assignor to The Westmoreland Chemical and Color Co., Philadelphia, Pa. U.S. Pat. 1,186,611, June 13, 1916. Date of appl., Apr. 16, 1913.

BASIC ferric sulphate is produced by adding barium hydroxide to a solution of ferric sulphate, dissolving the precipitated ferric hydroxide in excess of the sulphate solution, and filtering to remove barium sulphate.—A. B. S.

*Cyanogen compounds; Synthetic production of* —. A. R. Lindblad, Ludvika, Sweden. U.S. Pat. 1,186,921, June 13, 1916. Date of appl., Nov. 18, 1914. SEE Eng. Pat. 22,852 of 1914; this J., 1915, 905.

*Sodium sulphate and cement; Process and apparatus for manufacture of* —. L. P. Basset, Paris. Eng. Pat. 8128, June 1, 1915. Under Int. Conv., June 11, 1914.

SEE Fr. Pat. 477,353 of 1914; this J., 1916, 601.

*Salt; Process and apparatus for converting rock salt into a bulky table* —. L. W. Damman, Zwolle, Netherlands. Eng. Pat. 9082, June 21, 1915. Under Int. Conv., June 29, 1914. Addition to Eng. Pat. 10,304 of 1914, dated Sep. 17, 1913.

SEE Ger. Pat. 291,265 of 1914; this J., 1916, 690.

*Zinc sulphate solution from zinc ores; Process of preparing pure* —. S. Araki, Osaka, Japan. U.S. Pat. 1,185,757, June 6, 1916. Date of appl., Sept. 6, 1913.

SEE Fr. Pat. 464,038 of 1913; this J., 1914, 484.

*Nitrogen; Fixation of* —. E. A. Ashcroft, London. U.S. Pat. 1,186,367, June 6, 1916. Date of appl., Dec. 21, 1914.

SEE Eng. Pat. 10,420 of 1914; this J., 1915, 716.

*Furnaces and kilns for applying and utilising heat of combustion.* Eng. Pat. 4226. See I.

*Treatment of waste sulphuric acid from the refining of tar oils or petroleum.* Ger. Pat. 291,775. See III.

*Process for obtaining cement and soluble potassium compounds.* U.S. Pat. 1,186,522. See IX.

*Manufacture of caustic magnesia from crystalline magnesite.* Ger. Pat. 291,686. See IX.

*Manufacture of fertilisers containing ammonium chloride or pure ammonium chloride.* Ger. Pat. 292,174. See XVI.

*Manufacture of a fertiliser from the waste liquor from potash works.* Ger. Pat. 292,209. See XVI.

## VIII.—GLASS; CERAMICS.

*Potassium chlorate or perchlorate as substitute for nitre in the glass industry.* L. Springer. Sprechsaal, 1916, 49, 96—97, 104—105. Z. angew. Chem., 1916, 29, Ref., 304—305.

EXPERIMENTS on a working scale have shown that nitre may be replaced by potassium chlorate or perchlorate. In consequence of the volatility of potassium chloride, it is necessary to add also sodium or potassium carbonate to maintain the desired viscosity and composition of the glass. In small-scale tests with lead glasses a slight opalescence was produced, probably owing to the action of volatilised potassium chloride.—A. S.

*Silver on glass; Yellow coloration of burnished* —. L. Springer. Keram. Rundsch., 1916, 24, 89—90, 95—96. Z. angew. Chem., 1916, 29, Ref., 306.

IN continuation of earlier work (this J., 1916, 539), it has been found that in using silver decoration in conjunction with enamel colours, it is immaterial whether the silver be applied first and fixed by burning and then the enamel applied and the ware fired a second time, or the silver and enamel applied and both fixed together by a single firing. Yellow coloration of the silver and discoloration of the enamel are not to be feared if pure silver is used, with lead borate as flux.—A. S.

*Flint and quartz; Studies on* —. I. J. W. Mellor and A. J. Campbell. Trans. Eng. Ceram. Soc., 1915-16, 15, 77—85.

CRYSTALLISED silica occurs in nature as:  $\alpha$ -Quartz, sp. gr. 2.65—2.66,  $\alpha$ -tridymite, sp. gr. 2.32—2.33, and  $\alpha$ -cristobalite sp. gr. 2.31—2.32. By heat these are changed into other forms, the equilibrium condition of all different forms between 1470° C. and the melting point, 1625° C., being  $\beta$ -cristobalite. The specific gravity of quartzose silica on calcination falls from 2.66 to 2.32, and that of potters' flint from 2.61 to 2.22. When calcined in a china biscuit oven at cone 10, the change from the high to the low specific gravity form is rapid in the case of flint, and slow in the case of quartz; the rates of change are about as 1 is to 3. The calcined products contain different proportions of two substances, which may be designated A- and B-quartz or flint. The reactions appear to be unimolecular. The relation between the specific gravity of flint and quartz and the number of times (n) they have been fired in a china biscuit oven is given by the equations:—

$$S(\text{flint}) = \frac{14.87}{6.7 - e^{-1.06n}} \text{ and } S(\text{quartz}) = \frac{18.096}{7.8 - e^{-0.314n}}$$

Calcining for 3 hours at cone 35 converts about 65% of A-quartz into B-quartz, but in the same time at cone 14 nearly all the A-flint is converted into the B-variety. At cone 3 about 35% of grey flint and about 30% of black flint is converted. The decrease in specific gravity is accompanied by a corresponding increase in volume of quartz and flint on calcination, and the latter is shattered much more than the former by the process. Calcined flint and quartz, containing different proportions of the A- and B-forms of silica, naturally do not behave quite the same in pottery bodies. —W. C. H.

*Flint and quartz; Studies on* —. II. J. W. Mellor. Trans. Eng. Ceram. Soc., 1915-16, 15, 86—102.

A BRIEF outline of the geology of flint formation is given and the method of collection of potters' flints is described. These are divided into "chalky" flints—the outsides of which are coated with a white layer, which differs only from the main mass in composition in containing about 8% of calcium carbonate—and "boulder" flints. Geologically and chemically there is no essential difference between them. The colour of grey and black flints appears to be due to hydrocarbons. Partly for the sake of removing this colour, flints are calcined for pottery purposes, and if the process is complete the specific gravity of the material is reduced from about 2.61 to 2.22. Incomplete calcination yields a material having an intermediate value for the specific gravity and a table and method of calculation are given by which the percentages of high- and low-gravity flint in a sample can be determined from its specific gravity. Differences in calcination further affect the slip weight of flint; the greater the specific gravity of a sample of calcined flint, the less will be the dry contents of the slip. The substitution

of sand for flint is said to cause peeling or crazing. These faults may be due to sand being underground, owing to its toughness when uncalcined, or to the difference in the specific gravities of sand and calcined flint, which would affect the weight per unit volume of the slip and so cause a smaller quantity of sand to be introduced into the body. Several formulae and diagrammatic representations for slip weights of slip are also given.—W. C. H.

*Flint and quartz; Studies in —.* III. B. Moore and J. W. Mellor. Trans. Eng. Ceram. Soc., 1915-16, 15, 103—116.

OWING to a possible shortage of flints, the authors have considered other available supplies of silica which might be suitable for bodies, the chief desideratum being a satisfactory colour when fired. Among fairly pure forms of silica are sand, geyserite (though this is obtained from Iceland, and consequently is not a British material), chert, samples of which, however, so far have not been found to fire a good colour, and quartz and quartzite rock. It is probable that the speed of reaction of flint with felspar and clay differs from that of quartz. Uncalcined sand is tougher and so requires more grinding to make it strictly comparable with calcined flint. When extra finely ground quartz is substituted for flint, the margin of safety from crazing is increased, but the percentage of cracked biscuit also increases very much. Similar results are obtained when Westwood stone is substituted for Cornish stone and flint, and no economy is effected; partial replacement of Cornish stone by more silicious rocks such as Washerwall or Westwood stone is hardly a case of a substitute for flint. Flint in body mixtures may also be dispensed with by partially replacing china and ball clay by some more silicious clay, such as silicious china and ball clays, pipe clays, etc. Many of these are white burning and comparatively highly plastic.

—W. C. H.

*Fireclays; The effect of loads on the refractoriness of —.* J. W. Mellor and B. J. Moore. Trans. Eng. Ceram. Soc., 1915-16, 15, 117—130.

THE lowering of the fusing point of refractory materials by pressure may be due to pressure diminishing the apparent viscosity or to its hastening the reaction between different minerals in the clay. The authors used an electric resistance furnace in their tests. It consisted essentially of a graphite resistance packed round a refractory cylinder open at both ends; test-pieces were supported on blocks just inside the lower end and pressure could be exerted on the pieces by means of a thick graphite rod worked by a lever to give varying pressures. The test-pieces were cylinders 6 cm. long and 2 cm. diameter and were fired to cone 4. The rate of heating the furnace was about 50° C. in 5 mins., and the temperatures were measured by Seger cones. It was found that the softening or "squatting" temperature of fireclays is reduced by a compressive load, and the decrease, with unit increase of load, is directly proportional to the squatting temperature, and equal to  $k$  times the squatting temperature. The relation between the squatting temperature  $T$  (expressed either in degrees C. or in Seger cones) and the load  $W$ , expressed in pounds per square inch, is given by the equation:  $T = Ce - kW$  where  $C$  represents the squatting temperature, without load,  $k$  is a constant dependent upon the particular clay, etc., and  $e$  is the regular exponential constant. The squatting temperature of china clay falls approximately one cone for every 5½ lb. per square inch increase in the load. The more silicious the clay, the less is the difference between the squatting temperatures with and without load.—W. C. H.

*Chrome-tin pink; A note on —.* J. W. Mellor. Trans. Eng. Ceram. Soc., 1915-16, 15, 131—132.

THE author considers that the tint of chrome-tin pink is the same whatever compound of chromium is used, and that differences observed by other workers arose from incomplete development of the colour through under-firing. To test this point, four portions of the same mixture were fired one at cone 06a, one at cone 4, and one at cone 10, whilst the fourth was fired at cone 10, ground, and refired at cone 10. The samples were ground, washed, mixed with 85% of slop glaze, and fired in the majolica kiln. The colours were analysed by Lovibond's tintometer with the following results:—

Pink matured at :	Red.	Yellow.	Blue.
Cone 06a .....	1.15	2.8	—
Cone 4 .....	8.2	9.0	1.0
Cone 10 .....	18.5	16.0	1.5
Cone 10 repeated ...	18.5	16.0	3.0

These figures show that at least for the particular chromium compound employed, the tint, during development, is sensitive to the temperature, and the reaction is virtually complete after once firing to the temperature of the china biscuit oven. If the calcination is stopped before the pink is fully developed, the tint is probably dependent on the source of chromium employed. The figures also show that purpling of the chrome-tin pink occurs when the colour is fired at too high a temperature.—W. C. H.

*Brown [earthenware] colours; Studies on the —.* I. J. R. Adderley. Trans. Eng. Ceram. Soc., 1915—16, 15, 133—134.

EXPERIMENTS were made to show the effect of varying proportions of china clay and zinc oxide on a mixture of equal parts of ferric and chromic oxides. These mixtures were calcined, wet ground, sifted through a 200's lawn, dried, and painted on earthenware biscuit. The colours were hardened on, and dipped in (1) raw lead, (2) fritted lead, and (3) leadless glaze, and fired in the earthenware glost oven. The raw lead glaze gave the worst results, as it attacked the chromic and ferric oxides at different rates and so produced irregular variations in the colours. The fritted lead glaze gave the best results, and apparently did not attack the constituents at different rates. The tests showed the characteristic zinc-iron brown as the amount of zinc was increased, and much darker tints were developed as the amount of china clay was increased.—W. C. H.

#### PATENTS.

*Glass; Method of marking —.* The British Thomson-Houston Co., London. From General Electric Co., Schenectady, N.Y., U.S.A. Eng. Pat. 12,617, Sept 2, 1915.

THE surface of the glass is first covered with colloidal thorium or tungstic oxide and the coated surface is marked in the desired manner with a stylus of aluminium, magnesium, copper, brass, soft iron, nickel, platinum, gold, or other soft metal, depending on the colour desired. The article may subsequently be subjected to the action of colouring baths. The colloidal layer enables the stylus to "bite" the glass, which thereupon becomes deeply scratched, and particles of abraded metal adhere firmly to its surface and remain when the colloidal coating has been washed off; they are not removed by ordinary friction or washing but may be removed by solution in acid, leaving distinct markings on the glass.

—A. B. S.

*Glass; Manufacture of*—J. A. Chambers, Pittsburgh, Pa. U.S. Pat. 1,186,076, June 6, 1916. Date of appl., Jan. 26, 1916.

THE molten glass metal, at a flowing or dipping temperature, is transferred to a refractory receptacle and maintained at a temperature sufficiently high to eliminate bubbles in the glass.—A. B. S.

*Glass furnace.* W. Westbury, Assignor to L. S. Skelton, Okmulgee, Okla. U.S. Pat. 1,187,025, June 13, 1916. Date of appl., Nov. 12, 1915.

A GLASS furnace has a "dog-house" projecting internally and externally from the line of the front wall and terminating below the crown of the furnace. The top wall of the dog-house has a draw-hole extending equally on opposite sides of the line of the front wall, the latter having a breast curved to form a recess communicating with the inside of the draw-hole.—A. B. S.

*Abrasive materials; Manufacture of*—T. B. Allen, Toronto, Canada, Assignor to General Abrasive Co., Niagara Falls, N.Y. U.S. Pat. 1,187,225, June 13, 1916. Date of appl., Apr. 19, 1915.

BAUXITE containing iron oxide, silica, and titania, is fused in an electric furnace with a quantity of carbonaceous material sufficient to reduce the iron oxide and silica, and part of the titania. The abrasive material and ferro-silicon produced are tapped off at different levels, and the abrasive material is cast into ingots.—A. B. S.

*Porcelain, earthenware, etc.; Production of a coating of metallic appearance on*—Lindner und Co., Jecha. Ger. Pat. 292,105, Oct. 9, 1915.

A BLACK sharp-fire glaze is first produced on the article, which is then painted with a suitable stain, and again fired in a muffle-kiln.—A. S.

*Clay and kaolin slips; Purification of*—Richter und Richter, Frankfurt. Ger. Pat. 291,834, Aug. 31, 1913. Addition to Ger. Pat. 258,152 (see Fr. Pat. 443,789 of 1912; this J., 1912, 1005).

THE method of preparing clay for the purification of effluents, etc., as described in the chief patent (*loc. cit.*), is applied to the purification of clay and kaolin slips, for the purpose of removing sandy constituents and increasing the adsorptive power of the clay.—A. S.

*Refractory materials applicable as electric resistances.* W. R. Just, Freiberg, Assignee of M. Fraenken, Grunewald, Germany. Eng. Pat. 4080, Mar. 15, 1915. Under Int. Conv., Mar. 23, 1914.

A MIXTURE of equal parts of commercial zirconia and coarse carborundum (silicon carbide) is fashioned by customary methods and burned at a high temperature. With such a mixture the tendency of zirconia to crack and lose mechanical coherence is not observed, and the carborundum is protected from oxidation. A chemical reaction appears to occur between the zirconia and carborundum; the articles shrink considerably during burning and become covered with a glaze-like layer. The material is stated to be specially applicable to the manufacture of muffles, crucibles, and furnace linings and for electric resistances used at high temperatures.—A. B. S.

*Grinding wheels; Treatment of the material for use in the construction of*—E. Gerbel-Strover, Westminster. Eng. Pat. 10,328, July 15, 1915.

GRIT material, composed of alumina or fused bauxite (artificial corundum) is heated to 130° to 180° F. (54°—82° C.) and mixed with 20 to 25% of its weight of nitre-cake (sodium bisulphate) which has been heated to 250° F. (121° C.) so that the grains of grit may be uniformly coated. The product is spread in layers, roasted at a sufficiently

high temperature to produce sulphuric anhydride, and then washed. This treatment removes iron oxide, titania, and free carbon. The purified grit is used for making grinding wheels.—A. B. S.

*Bricks or tiles; Regenerator*—C. R. Payne, Leeds, and E. Linsley, Horsforth. Eng. Pat. 12,279, Aug. 26, 1915.

*Fire bricks; Manufacture of*—M. Curry, Cornsley Colliery, and W. O. Wood, South Hetton, Durham. Eng. Pat. 12,756, Sept. 6, 1915.

*Manufacture of antimonates for clouding glasses and enamels.* Eng. Pat. 11,083. See VII.

## IX.—BUILDING MATERIALS.

*Portland cement.* G. A. Rankin. J. Franklin Inst., 1916, 181, 747—784. (See also this J., 1915, 139.)

THE author attributes the superiority of Portland cement to the presence of 35% of tricalcium silicate. Study of the ternary system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (this J., 1915, 139) indicates that the formation of the constituents of Portland cement is as follows:—The calcium carbonate is first converted into free lime which then unites with the clay forming  $5\text{CaO}, 3\text{Al}_2\text{O}_3$  and  $2\text{CaO}, \text{SiO}_2$ ; these subsequently unite with more lime and form  $3\text{CaO}, \text{Al}_2\text{O}_3$  and  $3\text{CaO}, \text{SiO}_2$ , the reaction being facilitated by the formation of a flux at 1335° C.—the eutectic temperature of  $2\text{CaO}, \text{SiO}_2$ ,  $5\text{CaO}, 3\text{Al}_2\text{O}_3$ , and  $3\text{CaO}, \text{Al}_2\text{O}_3$ . As the temperature rises above 1335° C. any free lime present reacts with the  $2\text{CaO}, \text{SiO}_2$  forming  $3\text{CaO}, \text{SiO}_2$ . It is not necessary to continue the heating to complete fusion, a temperature of 1650° C. being usually sufficient for commercial materials. At this temperature the mass consists of 30% molten and 70% solid material, but on cooling the clinker is completely crystalline, and contains approximately  $3\text{CaO}, \text{SiO}_2$ , 45%,  $2\text{CaO}, \text{SiO}_2$ , 35%, and  $3\text{CaO}, \text{Al}_2\text{O}_3$ , 20%. The percentage of  $3\text{CaO}, \text{SiO}_2$  is the chief factor in determining the value of a Portland cement. This is the last substance to be formed during the heating of the materials and under ordinary conditions 35% of it is the maximum obtained. The proportion is regulated by the temperature and duration of the heating, the amount of fluxing agents ( $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ , etc.) present, and the size of the particles. A larger proportion of free lime than that normally used would produce a higher percentage of  $3\text{CaO}, \text{SiO}_2$  if the temperature and duration of heating were sufficient, but free lime in the finished cement must be avoided as it causes loss of strength and facilitates disintegration. As an alternative to a higher burning temperature (which is impracticable commercially), a material richer in fluxes may be used, so as to bring about the reaction  $\text{CaO} + 2\text{CaO}, \text{SiO}_2 = 3\text{CaO}, \text{SiO}_2$  below 1650° C. instead of at the much higher temperature required with the usual materials. It is proposed to study other systems such as  $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  to ascertain whether the replacement of  $\text{Al}_2\text{O}_3$  by other oxides will effect this reduction in temperature and increase the rate of formation of  $3\text{CaO}, \text{SiO}_2$ .—A. B. S.

*Nature of the sulphur in moorland soils injurious to plant growth and subterranean structures.* Thömer. See XVI.

## PATENTS.

*Timber; Treatment of*—W. Powell, London. Eng. Pat. 9044, June 19, 1915.

TIMBER is impregnated with a solution of sugar (sp.gr. 1.080) to which has been added about 5% of another carbohydrate (such as starch or dextrin) and 0.5% of gum tragacanth, with or

without 3% of arsenic, at a temperature between 120° and 140° F. (49°–60° C.) and afterwards at boiling point. It is allowed to cool to 110° F. (43° C.) in the solution and is then taken out and dried. The sugar thickens the fibres of the wood, strengthening them and increasing their tenacity and lessening the pores; the other carbohydrate reduces the susceptibility of the wood to moisture and increases its strength and tenacity; the arsenic preserves it from the attacks of white ants and other insects.—A. B. S.

*Plastic [paving] composition and process of making same.* G. A. Henderson, St. Albans, W. Va. U.S. Pat. 1,187,314, June 13, 1916. Date of appl., Nov. 30, 1914.

SHREDDED wood, in particles of various shapes and sizes, is freed from all extractive matter; the particles are abnormally enlarged and partially dried. They are then graded so that the major portion consists of particles ranging from  $\frac{1}{4}$  in. by  $\frac{1}{4}$  in. down to impalpable dust, the latter representing 2–3% of the total; these are mixed with the larger sizes, so that the ultimate volume is equivalent to 70–90% of the ungraded volume. The mixture is agitated with a preservative binder, previously heated to 300° F. (about 150° C.), until the particles have absorbed the binder into their expanded pores to a predetermined proportion (e.g., 25–40% by vol., measured cold). The mixture, when at 250° F. (about 120° C.), is exposed to a cooling effect to contract the ingredients, so that the binder is entrapped within the contracted pores, completely filling them, and the mass, while cooling, is gradually compressed to 50% of its contracted volume. To determine the correct quantity of binder, the pores within and the spaces between the woody particles, when treated, expanded, and graded, are measured, and the result subtracted from 100, giving the percentage volume of solids; the latter figure is subtracted from 50 and 7–10% added to the result.—J. F. B.

*Building material; Cementitious*—. M. Rüdiger, Hamburg. Ger. Pat. 292,104, June 13, 1914.

A MIXTURE of magnesia, magnesium sulphate, kieselguhr, and trass, with filling materials which do not putrefy or swell, can be used as a cement which sets to a stone-like material, resistant to water. The product, even with iron reinforcement, is lighter than water.—A. S.

*Bricks of uniform deep red colour; Production of*—. J. Marz, Frankfurt. Ger. Pat. 292,187, June 18, 1914.

THE moist bricks, direct from the press, are arranged in pairs, and pressed tightly together, with a sheet of air-tight paper between the faces of the bricks. The double bricks are dried, burnt, and then separated. By excluding air and combustion gases from the face of the bricks in this way, a deep, uniform red colour is developed on the protected surfaces and extends to a sufficient depth for practical purposes.—A. S.

*Plastic material and composite accelerating material therefor. Cementitious material. Composite strength-accelerating material.* E. L. Conwell, Upland, Pa., Assignor to Aluminate Patents Co., Philadelphia, Pa. U.S. Pats. (A) 1,185,773, (B) 1,185,774, and (C) 1,185,775, June 6, 1916. Date of appl., Nov. 7, 1912.

(A) A HYDRATED high-calcium lime is mixed with 10 to 30% of natural cement which has been ground with 5 to 15% of "sodium persulphate energising material." (B) A rich hydrated lime is mixed with 10 to 20% of fused "calcium aluminate strength accelerating material com-

prising considerable silica," which has been ground with one-eighth as much sodium persulphate energising material. (C) A dry, finely divided composite material for accelerating the strength and improving the plasticity and cementitious properties of cement and plaster, consists of fused "calcium aluminate strength-accelerating material including silica" which has been ground with about one-eighth as much sodium persulphate energising material.—A. B. S.

*Cement and soluble potassium compounds; Process for obtaining*—. C. Ellis, Montclair, N.J., Assignor to Ellis-Foster Co. U.S. Pat. 1,186,522, June 6, 1916. Date of appl., Jan. 29, 1916.

POTASSIUM-BEARING silicious material is incorporated with calcareous material and calcium chloride and fused at about 1300° C. Potassium chloride is formed, volatilised, and collected. The molten non-volatile residue, after being sprayed with water and finely ground, is a hydraulic cement.—A. B. S.

*Magnesia; Manufacture of caustic— from crystalline magnesite.* Austro-American Magnesite Co. (Oesterr.-amer. Magnesitges.), Radentheim, Austria. Ger. Pat. 291,686, Oct. 3, 1913. Under Int. Conv., Sept. 30, 1913.

THE magnesite is burnt at as low a temperature as practicable, and the rate of dissociation of the magnesium carbonate is increased by adding steam to the atmosphere in the kiln. In this way caustic magnesia of high activity, suitable for the production of oxychloride cements from magnesium chloride liquors, can be obtained from crystalline magnesite.—A. S.

*Sintered magnesite; Manufacture of*—. Harburger Chem. Werke Schön und Co., Harburg. Ger. Pat. 291,913, Oct. 6, 1915. Addition to Ger. Pat. 288,262 (this J., 1916, 180).

A MIXTURE of lime, iron oxide, and alumina, to which suitable additions may be made to obtain a mixture containing 2–4% SiO<sub>2</sub>, is used to decompose the magnesium chloride liquor. The mixture should contain 1.5–5% Fe<sub>2</sub>O<sub>3</sub> and 0.5–1.5% Al<sub>2</sub>O<sub>3</sub>, and such a quantity is used that the precipitate does not contain more than 5% (calculated on the dry substance) of free lime.—A. S.

*Wood; Method of increasing the density of*—. F. and H. Pfeumer, Dresden. Ger. Pat. 291,945, June 26, 1915.

THE wood is subjected to pressure on all sides whilst surrounded by an elastic or viscous medium (pitch, asphalt, resins, thick glue solution, etc.) at 90°–150° C. The hardness and density of the wood are increased, and the treated wood will take a better polish.—A. S.

*Wood; Process of treating*—. L. Petersen-Hviid, Kastrup, Denmark. U.S. Pat. 1,186,604, June 13, 1916. Date of appl., Dec. 30, 1913.

SEE FR. Pat. 466,768 of 1913; this J., 1914, 965.

*Coating composition for concrete and cement.* U.S. Pat. 1,179,413. See XIII.

## **X.—METALS; METALLURGY, INCLUDING ELECTRO-METALLURGY.**

*Semi-steel; The nature and uses of*—. I. I. Howell. Proc. Brit. Foundrymen's Assoc., 1914-15, 235–244.

STEEL, when melted in a cupola, begins to take up carbon at a blood-red heat, and continues to do so until there is sufficient present to bring the melting

point down to the temperature of the melting zone. The preparation of the coke bed is important for good cupola working, and, when using medium-weight coke, small pieces should be closely packed, the steel being then charged in first, in direct contact with the coke, following up with the iron. The steel should be charged into the middle of the cupola, to avoid oxidation and also action on the lining. These points affect considerably the quantity of slag, which is formed in greater quantity in melting semi-steel than with ordinary cast irons. The addition of steel to cast iron has a tendency to increase the hardness of the resulting metal, and in calculating mixtures for the production of semi-steel, the best results are obtained with:—phosphorus, 0.35 to 0.45% or lower; sulphur, 0.025 to 0.035%; and manganese, 1% or higher. The silicon should be from 1.65 to 1.75%, and ferro-manganese should be added to bring the manganese up to 2.0 to 2.5%, as from 1 to 2% is lost in the cupola. Increased tensile strength can only be obtained by addition of steel to low-grade irons; the addition of steel to strong irons, whilst increasing the hardness, decreases the tensile strength. Microscopic examination of a semi-steel, that has passed the point of hardness giving the greatest strength whilst the material is still machinable, showed the cementite in small and regular areas throughout, with almost entire absence of pearlite, and the phosphide eutectic in regular pools surrounding the cementite. When strength is a secondary consideration and wearing properties under high temperatures important, this structure is most desirable.—B. N.

*Iron; Thermo-electric measurement of the critical points of*—G. K. Burgess and H. Scott. *Comptes rend.*, 1916, 163, 30—32.

THE investigation was made with very pure iron (99.968% Fe) by a modification of the thermo-electric method employed by Boudouard and Le Chatelier (this J., 1904, 20; *Rev. Mét.*, 1, 134). The  $A_1$  and  $A_2$  points were clearly indicated on both heating and cooling curves, the former at 768° C. and the latter in the vicinity of 880° C. In the thermo-electric method employed by Benedicks (this J., 1916, 362) the  $A_2$  point was clearly defined at 875° C. but no indication of the  $A_2$  point was obtained.—W. E. F. P.

*Iron-carbon diagram; Position of martensite in the*—W. Broniewski. *Comptes rend.*, 1916, 162, 917—919.

COMPARATIVE experiments on the E.M.F. of solution of annealed steels containing varying proportions of carbon, and of the same steels after quenching at 900° C., show that the dissolving of the carbon in the form of martensite reduces the free energy of the ferrite, and the order of magnitude of this diminution of free energy has been calculated. Martensite is regarded as a solid solution of carbon (or cementite) in  $\alpha$ -iron, as maintained by Le Chatelier, and the experimental results are considered to indicate that the temperature region within which it is stable is below that of annealed steels. The limiting concentration of the solid solution (less than 0.05% C at the ordinary temperature) increases as the temperature falls and becomes rapidly larger when the temperature of liquid air is approached; this is shown in an equilibrium diagram. The appearance of martensite in a state of unstable equilibrium, as a result of quenching, is considered due to its being the form nearest to austenite (see Ostwald, *Z. physik. Chem.*, 1897, 22, 283).—F. Sodn.

*Steel; Some properties of annealed*—T. Matsuda. *Sci. Rep. Tohoku Imp. Univ.*, 1916, 5, 121—126.

To determine the effects of varying annealing

temperatures on the properties of cold-drawn carbon steel (about 0.8% C), wires 20 cm. long and 1.8 mm. thick (about one-third the diameter of the original rod) were heated for 1 hour at from 47° to 755° C. and tested when cold. The tensile strength was practically constant up to 100° C., increased gradually to a maximum (about 5% above the value at ordinary temperature) at 200° C., and then decreased continuously, the decrease becoming much more rapid at 350° C. As regards torsion, the general features of the change were the reverse of those in the tensile tests, the minimum value occurring at 200° C. The solubility in 1% sulphuric acid (24 and 48 hour tests) was practically constant up to 500° C., but decreased rapidly beyond this point. No appreciable change in microstructure occurred up to about 400° C. For electrical resistance tests, wires 80 cm. long and 0.47 mm. thick were used; no perceptible change in resistance was found up to 200° C., but above this point a gradual reduction occurred until, at 400° C., a decrease of about 2% was observed. In the magnetic tests an external field of 267 gauss was applied; magnetisation began to increase from 100° C., attained a maximum (an increase of not more than 1%) at 200° C., and then gradually decreased. Additional experiments to determine the nature of the magnetic change in the vicinity of 200° C., indicated that the increase in tensile and decrease in torsional strength at this temperature is due to the magnetic transformation of cementite.—W. E. F. P.

*Steels; Transformations of special [alloy]—at high temperatures*. K. Honda, K. Tawara, and H. Takagi. *Sci. Rep. Tohoku Imp. Univ.*, 1916, 5, 135—151.

SIX carbon and six special steels were studied magnetically, thermally, and micrographically. The carbon steels contained from 0.1 to 1.22% C and were tested at temperatures up to 800° C. The special steels, the principal constituents of which are shown in the following table, were tested at various temperatures up to 1260° C.:

Name of steel.	C %	Si %	Cr %	W %	Mo %	V %
A. D.S.W. ....	1.16	2.89	2.74	—	—	—
B. Ultra Capital Siebhorn	0.66	0.48	3.43	16.81	—	0.11
C. New Capital Siebhorn	0.64	0.05	3.73	14.06	—	0.11
D. Böhler super rapid	0.82	0.18	3.71	14.63	0.017	0.20
E. Novo .....	0.59	0.22	2.86	18.81	—	—
F. Becker Diamond ...	1.05	0.18	—	3.17	—	—

For all the carbon steels the magnetic transformation of plain cementite was observed at about 200° C. both on heating and cooling. By the eutectic transformation the magnetisation was changed abruptly, the amount increasing with the quantity of eutectic. The eutectic point for heating was 30° to 80° higher than for cooling, and considerable heat was evolved or absorbed by the transformation. In the heating curves for steels A, B, and C, only two peaks occurred in the whole range of temperature up to 900° C., the first being due to the magnetic or  $A_2$  and the second to the  $A_1$  transformation; the positions of these peaks were independent of the maximum temperature to which the steels were previously heated. In the cooling curves for the same steels, the temperature of the beginning of the magnetic transformation was practically the same as that of its ending in the heating curves, but the  $A_2$  transformation was displaced towards a lower temperature, coinciding with the magnetic transformation in steel B but occurring slightly above the critical point in steels A and C. In the heating curves of steels D and E there were only two peaks, corresponding to the  $A_2$  and  $A_1$  trans-

formations, the positions of which were independent of the maximum temperatures previously attained. In the cooling curves, the critical point remained almost unaltered but the  $A_1$  and  $A_2$  transformations were coincident. When these steels were cooled from 1000° C. or above, the transformation was displaced to a much lower temperature (about 400° C.). Both on heating and cooling, steel F gave the magnetic transformation of plain cementite at about 200° C. in addition to a conspicuous heat phenomenon characteristic of the eutectic transformation. The existence of the latter was also shown by the magnetic experiments, the critical temperature being practically the same on heating and cooling. The conclusions drawn from the magnetic and thermal examinations were in all cases confirmed by the microstructures of the specimens.—W. E. F. P.

*Coke as a reducing agent in the electric smelting furnace.* R. C. Gosrow. Met. and Chem. Eng., 1916, 14, 691—694.

THE author describes attempts to smelt iron and manganese ores with coke in a three-phase furnace with four electrodes in a straight line. A large proportion of lime had to be used to eliminate a high content of sulphur in the coke. The furnace gave incessant trouble with crusts, hang-ups, broken electrodes, cold bottom, etc., although it had previously given good results when charcoal was used as the reducing agent. One important difference between coke and charcoal is that coke occupies only about one-third of the volume of the equivalent amount of charcoal. The volume of conducting material is thus reduced and the resistance of the charge increased. The controlling factor however in the action of coke is that the carbon is in the form of a dense hard structure in the mass forming the walls of the cell structure. This form of carbon is very resistant to oxidation, and also, at the temperature of the arc, gives rise to infusible carbides. This formation of carbides appears to be the principal objection to the use of coke in the electric smelting furnace. To it are due the "sowing" in the furnace, and the formation of accretions, with all their attendant evils. This trouble should be largely eliminated however where a nearly neutral or acid slag is used; bridging and "sowing" are much less marked in a low, stackless, type of furnace, than in the shaft and stack type.—T. St.

*Electric arc furnace for melting and refining steel; Some faults of the small —.* W. M. McKnight. Min. and Eng. World, 1916, 44, 955—956.

LOSSES may be caused by improper electrical conditions and by faulty design of the furnaces. The chemical conditions may be improved by employing a better refractory lining, producing an electrode that does not waste in heating the bath, and by utilising the waste gases. A basic lining of magnesite is recommended, either in the form of bricks conforming to the shape of the shell and embedded in a basic paste or coal-tar binder, or, preferably, the mass of magnesite is rammed into the shell. Graphite electrodes are preferable to carbon ones, as they have a greater carrying capacity, and may consequently be smaller in diameter, and offer less surface for radiation of heat and oxidation.—B. N.

*Heat treatment of steel in coal gas.* C. M. Walter. Midland Junior Gas Assoc., June 24, 1916. J. Gas Lighting 1916, 134, 691.

EXPERIMENTS on the case-hardening of steel showed that by using town's gas alone as a carburising agent very little carbon was absorbed by the steel, but if about 10% by vol. of ammonia was added to the gas very satisfactory results were obtained. One advantage of using gas

was that the quenching and re-heating could be carried out in an atmosphere of gas and so surface decarburisation was avoided.—W. H. C.

*Carbon in iron and iron alloys; Determination of total —.* F. Heinrich and K. Roger. Ferrum, 1916, 13, 81—84. Z. angew. Chem., 1916, 29, Ref., 287.

FOR the determination of carbon in iron by direct combustion in oxygen, an addition of aluminium, alumina, and lead peroxide is recommended. The aluminium facilitates the combustion owing to its high heat of oxidation, and the oxides accelerate the reaction, decompose carbides, and form a fusible slag. From 0.2 to 0.6 gm. of the sample is intimately mixed with about 2 grms. of a mixture of equal parts of aluminium powder, alumina, and lead peroxide, which has been dried at 300° C. From 0.7 to 0.9 gm. of lead peroxide is then added, according to the carbon content of the sample, and the mixture is placed in a boat, heated to 700°—800° C. in a Heraeus electric furnace, and then burnt in a current of purified oxygen. Combustion is complete in 5–6 minutes, and the carbon dioxide formed is absorbed by soda-lime.—A. S.

*Iron; New method of determining the gases in —.* P. Goerens and J. Paquet. Ferrum, 1915, 12, 57—73. Rev. Mét., 1915, 12, Ext., 402—404.

THE method consists in melting 3 grms. of the sample in an electric resistance furnace in a magnesia crucible with 3 grms. each of tin and antimony, and determining the gases evolved in an Orsat apparatus in which communication of the absorbent solutions with the outside air is prevented by mercury. Low-carbon steels produced in an electric furnace gave the smallest quantities of gas, a well deoxidised metal giving only 10 to 15 c.c. per 100 grms. Thomas and Martin steels gave from 22 to 78 c.c. per 100 grms. The limits found for the different gases were:—carbon dioxide 0.0020 to 0.0200, carbon monoxide 0.0015 to 0.1000, hydrogen 0.0002 to 0.0047, and nitrogen (by difference) 0 to 0.0141% by weight. Refined Thomas steel contains a smaller amount of gas than finished Martin steel. The authors also give the results of tests made at different stages in the manufacture of steels.—T. St.

*Sodium bisulphate; Pickling [steel] with —.* H. Le Chatelier and B. Bogitch. Rev. Mét., 1915, 12, 949—960.

THE authors have worked out the following procedure for utilising nitre cake as a substitute for sulphuric acid in steel pickling baths. The first solution is made to contain 25 grms. of sodium bisulphate per 100 c.c. and is used at 80° C. until half the sulphuric acid has been consumed; 12.5 grms. of bisulphate is then added and again half the acid is consumed; 12.5 grms. of bisulphate is again added, and the bath used a third time. The acid liquid thus charged with ferrous sulphate and on the point of crystallising is then discarded. Alternatively the bath may be cooled to 25° C., after adding a third lot of bisulphate, when the double sodium and iron salt which crystallises is separated, the liquor reheated to 80° C., and the volume made up with added water. To ensure that none is wasted, it is best to add the bisulphate dissolved in half its weight of boiling water. It is necessary to control the acidity of the bath by actual tests to avoid loss of bisulphate, on the one hand, and undue impoverishment of the bath, on the other.—T. St.

*Ammonium molybdate; Recovery of — from filtrates in the determination of phosphorus in steel and iron.* R. Friedrich. Chem.-Zeit., 1916, 40, 500—501.

THE filtrates from ammonium phosphomolybdate

precipitates are treated with sodium phosphate solution, the yellow precipitate formed is collected, washed with water containing sodium sulphate, and then dried in air; 500 grms. of the dried precipitate is dissolved in ammonia, 30 grms. of ammonium chloride and 60 grms. of magnesium chloride added, the ammonium magnesium phosphate separated by filtration, and the filtrate treated with concentrated hydrochloric acid, a few drops of hydrogen peroxide having been added previously if the solution has a greenish colour. An excess of hydrochloric acid should be avoided. The precipitated molybdic acid is collected, washed with water, dissolved in hot ammonia, and the ammonium molybdate allowed to crystallise. The mother liquor from these crystals is added to the next batch of molybdic acid filtrates to be treated; the liquor from the hydrochloric acid precipitation of the molybdic acid may also be saved for subsequent treatment.—W. P. S.

*Gold; Flotation of flour* — R. W. Smith. Eng. and Min. J., 1916, 102, 25—27.

AN ore containing Au 0.3 oz., Ag 2.5 oz. per ton, Pb 5, Zn 8.5, Fe 3.5, and Cu 0.5%, could not be treated with economic success by gravitation concentration, but was successfully dealt with by floating the slimes and treating the coarse portion by gravity and electrostatic separation. The froth concentrates, obtained without the use of acids or heat, were washed with water to a Wilfley table which effected a perfect separation of the relatively coarse lead and zinc. The gold, which was in an extremely fine state of division, appeared very largely in the first riffles of the table, the saving of gold amounting to about 85%.—T. Sr.

*Silver; Distribution of — between metallic lead and litharge-containing slags.* B. Dudley, jun. Met. and Chem. Eng., 1916, 14, 636—641, 695—701.

IN the assay of gold and silver ores where the precious metals are concentrated in a button of lead, loss may arise due to the solvent action of the slag for the gold or silver. The ebullition caused by the escape of gases formed in the reaction, and the convection currents set up in the molten slag, tend to produce the conditions necessary for each of the two immiscible solvents, lead and slag, to exercise fully its solvent action, and for equilibrium to become established. Experiments made by the author showed that with slags consisting of  $PbO$ ,  $Na_2O$ ,  $SiO_2$ , and  $B_2O_3$ , such an equilibrium may be established between the slag and lead with respect to silver, the total amount of silver retained by the slag being proportional to the weight of the slag under a given set of conditions. The concentration of silver in the slag increases with increasing temperature, other conditions being constant. The rate of increase of the silver concentrate is somewhat greater than the rate of the temperature increase. At constant temperature the concentration of silver in the slag varies directly with its concentration in the alloy with which the slag is in contact. For small concentrations of silver in the metal, the concentration in the slag is proportional to the weight percentage of the silver in the alloy. With richer silver-lead alloys the silver concentration in the slag is proportional to the molecular percentage of silver in the metal. Litharge is the most active of the slag-forming constituents in dissolving and retaining silver, the amount retained by the slag being directly proportional, other conditions being constant, to the molecular concentration of litharge in the slag, and independent of the silicate degree, or oxygen ratio of the slag. From the results obtained with slags the author has calculated the equilibrium concentration-ratios

of silver in silver-lead alloys and pure litharge at various temperatures. With regard to the retention of silver by litharge during cupellation, however it is pointed out that owing to oxidation of silver, the litharge produced may contain much more dissolved silver than corresponds to equilibrium conditions.—T. Sr.

*Zinc distillation process; The Roitzheim-Remy continuous* — M. Liebig. Metall u. Erz, 1916, 13, 143—156. Met. and Chem. Eng., 1916, 14, 625—629.

CONTINUOUS reduction is obtained by feeding the preheated charge of ore into the top of a vertical retort, and discharging the cooled residue mechanically from the bottom of a cast iron cooling chamber. The retort is open, top and bottom, but is sealed from the atmosphere by the charge and ashes. The clay condenser is arranged perpendicularly to the retort in a niche suitably heated, the front end being connected to a tube leading to the "prolong" catching the zinc dust, and the escaping carbon monoxide is burnt to ascertain if uncondensed zinc is present, the gases being passed into the main chimney. The furnaces are heated by gaseous fuel on the regenerative principle, and require little attention beyond superintendence of the machinery, and tapping of the zinc once in 24 hours. Zinc, of 98.6 to 99% purity, is obtained and is fairly free from lead. Several advantages, over the Rhenish smelting system, are claimed for the process, including the reduction, by 40%, of the labour required, the lessened consumption of refractory materials in muffles and condensers, equal to about 45%, and a saving in tools, machine work, heating coal and general costs, but against these economies there must be set the greater use of power for driving the discharging machinery, pumping cooling water, etc. The net result is stated to be, in the production of 15,700 metric tons, a saving of £407,000 (about £20,000). There are also the advantages of increased extraction, smaller mechanical losses of ore and metal, the furnaces have much less dead space, are easier to regulate and superintend, and the furnace room is free from fumes. The costs of installation of both systems, without the discharging machinery, are stated to be about the same, though the wear and tear on the parts of the machinery are so small that their ultimate cost is negligible.—B. N.

*Sherardising process.* O. W. Storey. Met. and Chem. Eng., 1916, 14, 683—691.

THE finely divided zinc used for the sherardising process is usually "blue dust," a zinc dust of extreme fineness in which each metallic zinc particle is covered with a film of oxide; a granular zinc-iron alloy of the composition  $FeZn_{10}$  is used to a limited extent. The coating formed consists of definite layers of iron-zinc compounds, and its structure depends on the time, temperature, and concentration of the zinc dust, employed in the operation. With a zinc dust low in metallic zinc a high temperature is necessary and alloys high in iron will be formed on the surface; with a rich zinc dust and a low temperature the alloy formed will be high in zinc and may have some free zinc on the exterior, though this layer of zinc will be thin. The author discusses the various theories which have been advanced to explain the sherardising process and concludes that it is principally a contact action made possible by the formation of intermetallic compounds. It is only at temperatures near the melting point of zinc that the vapour tension is high enough for the vapour to enter appreciably into the reaction. The action of  $FeZn_{10}$  in sherardising is not fully known, but there are indications that the compound is deposited as such on the iron. Sherardised coatings

may contain from 9 to 30% of iron; those high in iron (over 15%) are liable to become coated with red iron oxide on exposure. The best coatings turn deep grey, and finally black, due to the formation of magnetic iron oxide. Coatings may give poor results from being too porous, and should have a specific gravity of at least 6.75. A zinc dust having a high metallic content gives the best coating, and sherardising should be carried out at the lowest temperature economically possible, to secure a low iron content in the coating. The zinc dust should be frequently tested as to the metallic content and should be kept free from iron. The Preece test with copper sulphate gives excellent results for daily furnace-control tests. —T. St.

**Copper production of the United States.** Board of Trade J., July 6, 1916.

THE United States Geological Survey reports that the production of electrolytic, Lake, casting, and pig copper from primary sources, and the production of secondary copper by the regular refining plants in 1914 and 1915, was as follows:—

	1914.		1915.	
	Domestic.	Foreign.	Domestic.	Foreign.
<i>Primary.</i>	lb.	lb.	lb.	lb.
Electrolytic . . . . .	991,573,073	323,358,205	1,114,345,342	246,498,925
Lake . . . . .	158,009,748	—	236,757,062	—
Casting . . . . .	21,506,325	—	21,555,120	—
Pig . . . . .	39,334,043	—	15,047,890	—
<b>Total primary</b>	<b>1,210,423,189</b>	<b>323,358,205</b>	<b>1,387,705,523</b>	<b>246,498,925</b>
	1,533,781,394		1,634,204,448	
<i>Secondary.</i>				
Electrolytic . . . . .	27,702,928	—	38,156,789	—
Casting . . . . .	4,224,052	—	21,417,901	—
<b>Total secondary</b>	<b>31,926,980</b>	—	<b>59,574,690</b>	—
<b>Total output .</b>	<b>1,565,708,374</b>	—	<b>1,693,779,138</b>	—

The apparent consumption of refined new copper in the United States in 1915 was about 1,043,000,000 lb. In 1914 it was about 620,445,373 lb.

**Copper; Brittleness of annealed** — W. E. Ruder. J. Franklin Inst., 1916, 181, 859.

THE brittleness which occurs on heating copper and frequently ascribed to "burning" is due to deoxidation. With commercial copper brittleness first appears at 400° C. in dry hydrogen, at 600° C. in wet hydrogen, at 800°–850° C. in carbon monoxide, and at 700° C. in steam. Copper previously deoxidised by boron remains unaffected at all temperatures in a reducing atmosphere. The brittleness is attributed to the formation of a weak, spongy mass by the reduction of cuprous oxide around the copper grains. —A. B. S.

**Copper-zinc and copper-tin alloys; Structure of** — W. Broniewski. Rev. Mét., 1915, 12, 961–989.

THE author has made a résumé of the results obtained by various investigators in studying the different properties of the copper-zinc and copper-tin series of alloys, and concludes that the evidence indicates the existence of the compounds CuZn, Cu<sub>2</sub>Zn, CuZn<sub>2</sub>, and Cu<sub>3</sub>Sn, Cu<sub>2</sub>Sn, CuSn. The solid solutions obtained in the copper-zinc series are classified as follows:—*a*, solid solution of CuZn in copper; *β*, solid solutions round about CuZn; *γ*, solid solutions round about CuZn<sub>2</sub>; *δ*, solid solution of CuZn<sub>2</sub> in the modification of CuZn, stable at high temperatures; *ε*, solid solutions round about the modification of CuZn,

stable at low temperatures; *η*, solid solution of CuZn<sub>2</sub> in zinc. Those contained in the copper-tin series are classified as follows:—*a*, solid solution of Cu<sub>2</sub>Sn in copper; *β*, solid solution of copper in the modification of Cu<sub>2</sub>Sn stable at high temperatures; *γ*, solid solution of Cu<sub>2</sub>Sn in the modification of Cu<sub>2</sub>Sn stable at high temperatures; *δ*, solid solutions (very restricted) round about the modification of Cu<sub>2</sub>Sn stable at low temperatures; *η*, solid solutions of CuSn in Cu<sub>2</sub>Sn; *h*, solid solutions of Cu<sub>2</sub>Sn in CuSn.—T. St.

**Copper and tin; Transformations in alloys of** — in the solid state. M. P. Slavinsky. Rev. Soc. russe de Métal., 1913, 1, 548–563. Rev. Mét., 1915, 12, Ext., 405–409.

COPPER-TIN alloys with 57 to 77% Cu were cast in sand and cooled slowly. Observations on the transformations taking place in the solid state during heating and cooling were then made by the differential method. A diagram showing the results obtained is given. There is a marked discontinuity in the series at the composition Cu<sub>2</sub>Sn. The alloy of this composition is considered to be a true compound, and to undergo an allotropic transformation at 601° C. The alloys richer in copper give a variable arrest and also a constant arrest (497° C.). The first is considered to be due to the decomposition of the solid solutions, induced by the Cu<sub>2</sub>Sn transformation; as regards the second point, after the separation of excess of Cu<sub>2</sub>Sn, the final crystallisation consists of the simultaneous deposition of the saturated solid solution and of Cu<sub>2</sub>Sn. In the alloys poorer in copper than Cu<sub>2</sub>Sn there is a separation first of Cu<sub>2</sub>Sn and afterwards of Cu<sub>2</sub>Sn. The alloy corresponding to Cu<sub>2</sub>Sn has a single arrest at 680° C., considered to indicate the complete transformation of Cu<sub>2</sub>Sn to Cu<sub>2</sub>Sn and Sn.—T. St.

**Tin ores; Chemical assay of** — A. M. Matheson. Proc. Austral. Inst. Min. Eng., 1916, No. 21, 1–7.

THE percentage of tin in the battery pulp and primary and secondary tailings from a highly pyritic tin-stone was determined by vanning (after digestion with acid) and fusion with cyanide, and also by the Pearce-Low wet method (treatment with *aqua regia*, fusion with sodium hydroxide, reduction with nickel and hydrochloric acid, and titration with iodine solution). With the battery pulp, the average results by vanning were about 50% below those found by the chemical assay. Vanning the primary tailings gave a recovery of about 14.5%, but when 10 gm. (instead of 100 gm.) samples were taken, 50% of the tin content was recovered. With the secondary tailings, vanning gave 33% of the tin value as shown by the wet assay, but 50% when 10 gm. portions were used. In addition to being quick, the vanning method is valuable because it gives results which correspond roughly to those obtained in actual milling practice. Vanning for 15 mins. without acid treatment and in dirty water, showed that a slime table might be expected to save about 40% of the tin content of the primary tailings and about 48% of that of the secondary tailings. A Cornish round table actually operating on the latter made an average saving of 50%. The wet assay method has not been found to give too high results. The substitution of iron (horseshoe) nails for nickel in the reduction works well provided that two nails only are used.—E. H. T.

**Lead [sulphide]; Reactions during roasting of** — W. Reinders. Z. anorg. Chem., 1915, 93, 213–231. Chem.-Zeit., 1916, 40, Rep., 196.

THE roasting process consists of first incompletely roasting lead sulphide, and then heating the product with further amounts of sulphide without admission of air, but with removal of the



sulphur dioxide formed, until all the sulphur has been removed and the lead has separated. In this process, the lead sulphate first formed does not react with sulphide to produce lead and sulphur dioxide directly, nor are these products obtained by the interaction of lead sulphide and lead monoxide, but there are formed in succession the basic sulphates,  $(\text{PbO})\text{PbSO}_4$ ,  $(\text{PbO})_2\text{PbSO}_4$ ,  $(\text{PbO})_3\text{PbSO}_4$ , and finally,  $\text{PbO}$ . Lead sulphide and lead monoxide are not stable together, but give lead and basic sulphate. Lead reacts with normal lead sulphate with the formation of sulphide, but this reaction does not take place with basic sulphates. The pairs of phases  $\text{PbS} + \text{PbSO}_4$ ,  $\text{PbS} + (\text{PbO})\text{PbSO}_4$ , and  $\text{Pb} + (\text{PbO})\text{PbSO}_4$ , are stable, and give monovariant equilibria, when heated in closed tubes; only when the sulphur dioxide is withdrawn does the separation of the lead proceed. Pressure and temperature measurements have given, for the complete reaction, the equation  $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$ , —99,543 cal. The value calculated from the heats of formation is 95,230 cal. The separated lead retains a certain amount of lead sulphide in solid solution.—T. ST.

[Ore] flotation oils; Froths formed by —. W. A. Mueller. Eng. and Min. J., 1916, 102, 31—35.

THE froth produced by any given oil differs with the machine in which it is made. It is extremely important that the oil shall be well mixed with the pulp before flotation is attempted, the best way being to add the oils in the mills during grinding. When not thoroughly mixed, the oils prevent rather than produce froth, and for this reason extraneous oils such as cup greases and lubricating oils cause trouble in the flotation machines. *Pine oil*, as a general rule, is a rather poor mineral collector but a good frothing agent; it is, however, a good mineral collector on ores carrying chalcocite and on some zinc ores; its action as a mineral collector can often be increased by the addition of acid, and sometimes by the addition of caustic alkali; the froth is brittle, and the bubbles produced are small. *Coal tar* is a poor frothing agent but a good mineral collector, and is seldom used without mixing with pine oil or other frothing agent; it works well with many different minerals; it is difficult to mix with the pulp, and, in general, requires grinding; the bubbles are brittle. *Coal-tar creosote* is used chiefly to dilute the cheaper coal-tar oil, and for this purpose is very good; it is easy to mix; and works best on copper-bearing ores. The bubbles are very tough and tend to be rather large. *Wood creosote* resembles coal-tar creosote in some characteristics; it works best on zinc ores, and is often used to dilute coal tar in the treatment of these ores. The bubbles are even tougher than those yielded by coal-tar creosote. *Cresol* is used in small proportions in mixtures with coal tar. *Fuel-oil*, *pine-tar oil*, *oleic acid*, and *eucalyptus oil* are often used in mixtures. The best mixture can only be determined by trial, preferably on the large scale. In general, the best froth is one in which the bubbles are of medium size and rather tough.—T. ST.

[Ore] flotation; Use of oils in —. H. A. Megraw. Eng. and Min. J., 1916, 102, 50—56.

THE functions of a flotation oil are to reduce the surface tension of the liquid so that a more permanent gas bubble may be formed, and to oil the mineral particles preferentially. The oils used may be divided into two groups:—(1) those which serve to make frothing possible by reducing the surface tension of water, and (2) those which provide a non-wet film on the surface of the mineral particle. The best mixtures of oils to accomplish these results can only be deter-

mined by trial in each special case. The author describes investigations made to ascertain the best mixtures of oils for certain ores, and gives examples of actual practice.—T. ST.

Mercury ores in California; Concentration of —. F. Hamilton. Min. and Eng. World, 1916, 44, 997.

FRIABLE ores, in which the cinnabar is distinctly crystalline, have given a high extraction (above 90%) by water concentration on tables. Crushing by rolls produces a minimum of slimes, but if the pulp contains a cinnabar slime, either from "paint" ores or through fine crushing to release the sulphide, the extraction by tables is low. In such cases it may be improved by classification, and treating the different sizes on separate tables. The slimed cinnabar may be recovered by flotation, and a high extraction has been obtained with finely ground (80-mesh) ores, using either pine oil derivatives or eucalyptus oils, but the cinnabar should be "fresh," as on exposure it is oxidised sufficiently to affect results obtained by flotation.—B. N.

Manganese nitride; Magnetic susceptibility of —. T. Ishiwara. Sci. Reports, Tohoku Imp. Univ., 1916, 5, 53—61.

MANGANESE and nitrogen give rise to three ferromagnetic substances between 600° and 1600° C., two being nitrides, and the third probably a solid solution. One of these is  $\text{Mn}_3\text{N}_2$ , but the composition of the others has not been determined, though they may be differentiated by their characteristic thermo-magnetic curves and their critical points. Ammonia affects manganese in a manner similar to nitrogen at high temperatures, an exception being the formation of the paramagnetic nitride,  $\text{Mn}_2\text{N}_2$ . The existence of the ferromagnetic  $\text{Mn}_3\text{N}_2$ , described by Wedekind and Veit (Ber., 1911, 44, 263), has not been confirmed. The various values of susceptibilities for manganese, obtained by different physicists, may be explained as being due to the effects of nitrogen present in air or from other sources. The correct value of the susceptibility for pure manganese is given as  $\chi = 5.66 \times 10^{-6}$ .—B. N.

Carbon dioxide; Action of — on some metals and metallic compounds at a high temperature. F. von Bacho. Monatsh. Chem., 1916, 37, 119—123. Z. angew. Chem., 1916, 29, Ref., 279.

IF zinc sulphide be heated in a current of carbon dioxide, decomposition begins at 750° C., and increases with the temperature, the products being zinc oxide, sulphur dioxide, and carbon monoxide. Metallic copper when heated in carbon dioxide is attacked only when the metal begins to melt; cuprous oxide and carbon monoxide are formed. Metallic antimony is attacked at 830° C. At 1100° C. the following reaction occurs:  $2\text{Sb} + 3\text{CO}_2 \rightarrow \text{Sb}_2\text{O}_3 + 3\text{CO}$ .—A. S.

Cetraria islandica [Iceland moss] as a protective colloid. II. Colloidal gold. III. Colloidal palladium. A. Gutbier, J. Huber, E. Kuhn, and J. Kräuter. Kolloid-Zeits., 1916, 18, 57—71. Z. angew. Chem., 1916, 29, Ref., 270.

BY using an extract of Iceland moss as protective colloid (this J., 1916, 657), solid colloids containing high percentages of gold can be prepared, and so long as the gold content does not exceed 82%, these can be converted completely into the sol condition by means of water. Paal (this J., 1902, 994) obtained reversible gold colloids containing up to 93.41% Au, by using sodium lysalbinat as protective colloid, but in this case it is necessary to use an alkali solution to convert the solid colloid into the sol condition. Water sterilised by addition of chloroform was used in preparing the extract of Iceland moss, and it was

observed incidentally that water saturated with chloroform had a stabilising effect on some unprotected inorganic colloids. A protected colloidal gold preparation containing 42% Au showed no indications of ageing even after keeping for 1 month at 25° C. Colloidal palladium was prepared by reduction of palladous chloride by hydrazine hydrate in presence of an extract of Iceland moss; the limit of complete reversibility was attained at 70% Pd.—A. S.

## PATENTS.

*Iron and steel ingots; Moulds for casting*——. B. Talbot, Middlesbrough, and J. E. James, Marton-in-Cleveland. Eng. Pat. 100,549, Jan 19, 1916. (Appl. No. 888 of 1916.)

THE invention relates to composite moulds in which an annular channel is formed at the top for the reception of non-conducting material, with the object of keeping the upper part of the ingot fluid so long that it will flow down and fill the main portion of the cavity formed as the ingot solidifies.—T. St.

*Armour-plate; Process of forming*——. F. Conlin, Plainfield, N.J. U.S. Pat. 1,186,172, June 6, 1916. Date of appl., June 25, 1913.

THE face of a chill is covered with a plate of metal, and metal of relatively higher carbon content is poured on. The latter metal is harder and has a lower melting point than the plate-metal.—T. St.

*Removing oxide from the surfaces of articles of iron or steel; Electrolytic process for*——. P. Marino, London. Eng. Pat. 14,230, Oct. 7, 1915.

THE layer of iron oxide is removed by employing the articles as cathodes in an aqueous solution of phosphoric acid, or a compound of the acid to which free phosphoric acid has been added.—B. N.

*Iron or steel article; Metal-coated*——. C. Mark and C. Mark, jun., Evanston, Ill., Assignors to C. Mark, Chicago, Ill. U.S. Pat. 1,186,217, June 6, 1916. Date of appl., Aug. 4, 1915.

AN iron or steel article is coated with an alloy containing approximately Pb 94.45, Sn 3.74, and Zn 1.81%. The tin should be between 2 and 16%, the zinc between 0.80 and 5%, and the remainder lead, but the percentage of zinc should be less than that of tin. The coating, which is slightly electro-positive to iron, is applied in direct contact with the article.—T. St.

*Iron; Puddling*——. J. E. Fletcher, Dudley, and J. Harrison, Tipton. Eng. Pat. 7691, May 22, 1915.

CRUDE molten iron from a cupola or smelting furnace is treated in an intermediate refining furnace, at a medium temperature, until the carbon content is reduced preferably to 2.5–3% and the silicon, manganese, and phosphorus to below 0.5, 0.3, and 0.3%, respectively. After separation from slag, the semi-refined, molten metal is delivered, in separate portions, to a series of puddling or balling furnaces, in which a carburising atmosphere may be maintained if necessary, and finished as usual.—W. E. F. P.

[*Iron*.] *Puddling and basic open-hearth furnaces; Fix material for use in*——. J. F. Dery, New York. U.S. Pat. 1,175,933, Mar. 21, 1916. Date of appl., July 2, 1915.

A MIXTURE of finely divided iron ore or flue-dust, 9, lime, 1, and Portland cement, 2 parts by weight, is made fluid with water, poured into moulds, and allowed to set, the resulting blocks being afterwards allowed to dry slowly. The composition and exact proportions of the ingredients

should be such that the silica content of the finished material does not exceed 7%.—W. E. F. P.

[*Iron*.] (A). *Electric welding; Method of*——. (B) and (C). *Alloy for arc-welding*. D. H. Wilson, Paterson, N.J., and S. M. Rodgers, Pittsburgh, Pa. U.S. Pats. 1,187,410, 1,187,411, and 1,187,412, June 13, 1916. Dates of appl. (A) July 9, 1915, (B) and (C) June 16, 1915; all renewed May 10, 1916.

(A) THE welding metal is transferred continuously from the welding electrode to the work, across an arc produced by a current having a maximum potential sufficiently low to prevent pitting, formation of slag, and boiling or spattering of the material. (B) and (C). The welding metal consists of an alloy of iron (B) with about 1% Mn and a substantial proportion of copper, or (C) with more than 0.5% Mn.—W. E. F. P.

*Metal-coating baths; Protecting layer of refractory material for*——. O. van Raay, Ges.m.b.H., Kettwig. Ger. Pat. 292,031, May 9, 1915.

A LAYER of small balls of refractory material, e.g., glass, is used, which protects the bath from oxidation and prevents the coated metal cooling too quickly as it emerges from the bath, and thus facilitates the return to the bath of the excess of coating metal.—A. S.

*Cupolas and other furnaces; Safety device for*——. Akt.-Ges. R. P. Waagner, L. and J. Biro, and A. Kurz, Vienna. Eng. Pat. 6480, Mar. 14, 1914. Under Int. Conv., July 29, 1913.

A CAST-IRON cylinder provided at each end with a perforated dome is attached to the air-duct of the cupola. The upper dome is fitted with a safety valve which is kept closed by a spring until the pressure in the air-duct rises to an undesirable value by reason of stoppages in the blast tuyères and the like. When the valve is thus raised, the spindle actuates a lever which closes an electric circuit, and so rings an alarm. The lower dome is fitted with a valve which is kept open by a spring until the pressure inside the air-duct rises to a certain value. By this means a natural draught is provided in the cupola when the blast, for any reason is stopped, and prevents carbon monoxide from collecting in the air-duct. When the blast is again turned on, it blows first through the open valve into the atmosphere, and so clears the air-duct of any inflammable gases, then, when the pressure has risen sufficiently, the valve automatically closes and the blast passes into the cupola.—T. St.

*Gas furnaces [for melting metals]*. South Metropolitan Gas Co., and D. Chandler, London. Eng. Pat. 100,599, Jan. 3, 1916 (Appl. No. 10 of 1916.)

AN annular crucible, suitable for melting metals of high melting point, is heated by an atmospheric gas burner, the products of combustion passing up through the central aperture and then down over the outside to two superheaters for the combustible mixture, attached to the opposite sides of the furnace. Each superheater comprises an inner heating chamber provided with baffles, through which the mixed gas and air pass to the burner, surrounded by a casing provided with internal baffles through which the hot combustion products circulate to the flue.—W. F. F.

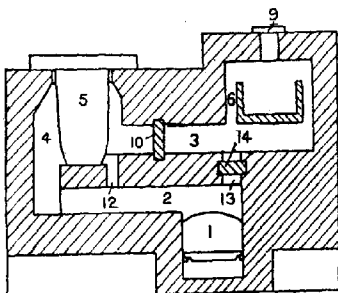
*Furnace*. W. M. Kelly, Anaconda, Mont. U.S. Pat. 1,186,104, June 6, 1916. Date of appl., Dec. 18, 1915.

TWO reverberatory furnaces are disposed in longitudinal axial alinement, thus forming a single treatment chamber, with means for firing at both

the opposite ends of the double furnace. A central transverse exit flue, in free communication with the furnace, surmounts and spans the roof of the latter, means being provided to control the discharge of waste gases from each end of the flue.—T. Sr.

*Salt-bath and preheating furnace; Combined* — Gebr. Pierburg, Berlin. Ger. Pat. 291,836, Aug. 3, 1915.

THE furnace (see fig.) is heated by coke, and the fire-gases pass from the combustion chamber, 1, through the flue, 2, to the chamber, 4, containing



the salt-bath, 5, and then return through the flue, 3, to the preheating chamber, 6; a portion of the fire-gases passes directly from the flue, 2, to the flue, 3, through the passage, 12, without passing through the chamber, 4. If desired, fire-gases may also pass directly to the preheating chamber through the passage, 13. Dampers are provided at 9, 10, and 14.—A. S.

*Roasting furnace; Mechanical* — S. Barth, Düsseldorf-Oberkassel. Ger. Pat. 291,886, May 24, 1914.

THE furnace is provided with a series of superposed rotating hearths, mounted on a central vertical shaft, and alternating with fixed hearths. The hearths are constructed of firebrick carried on a hollow iron framework, and air for cooling is circulated through the hollow shaft and frames. The charge is moved over the hearths by scrapers or the like to the openings leading from one hearth to the next, these openings being at the periphery in the case of the rotating hearths and at the centre in the case of the fixed hearths.—A. S.

*Shaft furnace for metallurgical purposes*. H. Rehmann and A. Mirbach, Düsseldorf. Ger. Pat. 292,004, May 10, 1914.

JUST below the arched crown of the shaft an annular dust separating and collecting chamber is formed by means of a low wall projecting from the inner wall of the shaft. This chamber communicates by passages in the crown with a second annular chamber above the latter. The furnace gases strike against the crown of the shaft and pass first into the lower and then into the upper dust-collecting chamber before being discharged. The dust chambers are provided with doors for cleaning purposes and with explosion doors. Passages lead from the bottom of the dust-collecting chambers through the wall of the shaft and open into the shaft lower down.—A. S.

*Refractory metal tubes*. The British Thomson-Houston Co., Ltd. From General Electric Co., Schenectady, N.Y., U.S.A. Eng. Pat. 8702, June 12, 1915.

TUBULAR bodies of refractory metal, such as tungsten or molybdenum, are prepared by placing

loose metallic powder in the annular space of a tubular mould between an inner flexible or elastic tubular wall, and an outer refractory rigid one, with open ends, a perforated tube supporting the flexible wall. The mould is placed in a container filled with liquid, so that pressure, applied to the liquid, is exerted uniformly in a radial direction upon the inner surface of the inner wall and against the outer wall. After removing the mould from the liquid, the flexible inner wall is detached, and the powder is baked in a furnace, whilst supported on the outer wall, to make it coherent, and then sintered by subjecting it to a high temperature before detaching it from the outer wall of the mould.—B. N.

*"Dental amalgam."* T. J. Davis, New York. Eng. Pat. 12,806, Sept. 7, 1915.

AN alloy of gold and other metals is subdivided into granules, and a coating of gold is applied to each granule. The resulting product is used for preparing the amalgam.—B. N.

*[Metal] leaf or foil; Decorative — and process of making the same*. W. J. Mellersh-Jackson, London. From Diamond Decorative Leaf Co., New York. Eng. Pat. 15,706, Nov. 6, 1915.

THIN pliable decorative leaf is produced by spraying on to a removable sized backing a thin layer of liquid material, comprising powdered aluminium, a colloidal protective substance, and a volatile solvent; in making artificial gold leaf, a tinting material of a yellowish or orange colouring matter is dissolved in the solvent. When dried slowly and uniformly, stratification takes place, the duplex leaf presenting a gold-coloured lustrous, metallic appearance on one face, and a silver-coloured appearance on the other.—B. N.

*Zinc; Recovery of* — F. W. Highfield, Whitechurch-on-Thames, Oxford. Eng. Pat. 9009, June 18, 1915.

IN an apparatus, other than that claimed in Eng. Pat. 6835 of 1914 (this J., 1915, 838), for condensing zinc vapour to liquid metal, the condensing chamber is divided into two compartments by a partition of fireclay, unglazed porcelain, carbon, or similar material impervious to molten zinc but pervious to carbon monoxide at the ordinary working temperature. The molten zinc is retained in the first compartment and removed periodically, while the carbon monoxide passes through the partition into the second compartment and is burnt therein, alone or with other gas, to maintain the necessary temperature. According to one method of carrying out the invention, eight zinc retorts are connected by radial pipes to a vertical, cylindrical condensing chamber having a concentric, vertical, porous partition by which the interior is divided into a closed, outer or annular compartment for retaining molten zinc, and a central compartment surmounted by a flue and provided with openings for the admission of air and combustible gas.—W. E. F. P.

*Zinc; Production of* — F. Tharaldsen, Drontheim, Norway. Ger. Pat. 292,471, Apr. 23, 1915. Addition to Ger. Pat. 286,229.

THE gases produced on treating the slag as described in the chief patent (this J., 1916, 185) are led into the condensing chamber connected with the furnace instead of into a separate chamber.—A. S.

*Aluminium; New metallic body consisting principally of —, and process of manufacturing the same*. A. J. de Montby, Paris. Eng. Pat. 16,359, Nov. 19, 1915.

SEE FR. Pat. 473,412 of 1914; this J., 1915, 558. The alloy to be added to the aluminium is prepared

by melting together 1.5 parts of cobalt, 12 of nickel, 0.25 of tungsten, 20 of silver, 2.25 of magnesium, and 70 of aluminium.

*Soldering paste.* H. Hess, Philadelphia, Assignee of C. E. Bonine, Melrose Park, Pa., U.S.A. Eng. Pat. 17,931, Dec. 23, 1915. Under Int. Conv., Oct. 15, 1915.

GLUE is added to a soldering paste containing solder powder, glycerin, and ammonium chloride, to prevent segregation of the ingredients on standing. When the paste is contained in collapsible tubes vaseline also is added to make the material flow easily under pressure. The most satisfactory results are obtained when a somewhat thick paste of the ingredients is baked for three hours at 50° C. before the full amount of glycerin necessary to bring the paste to its proper consistency is added. The paste contains solder powder 85.65 to 90.97, ammonium chloride 2.53 to 2.59, glycerin 5.43 to 5.85, and glue mixture 0.59%.—T. St.

*Metal and mineral bearing materials; Treating*——. J. L. Malm, Denver, Colo. U.S. Pat. 1,185,817, June 6, 1916. Date of appl., Feb. 21, 1911.

ORES, containing metallic sulphides, such as iron sulphide, are partially chlorinated to the extent of forming sufficient metallic chlorides, such as iron chloride, decomposable at low temperatures, so that, when heated, chlorine is liberated in amount sufficient to chlorinate substantially the entire remaining metallic contents of the ore. The metal from the decomposed chlorides is left in an inert condition.—B. N.

*Ores; Process of treating*——. R. S. Handy, Kellogg, Idaho. U.S. Pat. 1,185,902, June 6, 1916. Date of appl., Oct. 28, 1914.

SULPHIDE ores containing lead, silver, and zinc, are roasted, and then treated, whilst subjected to agitation and aeration, first with a hot aqueous solution of sodium chloride to extract the lead sulphate, and then with a hot aqueous solution of ferric chloride to extract the silver and zinc. The metal values are recovered from the resulting solutions.—T. St.

*Nickel anode and process of manufacture.* J. J. Walsh, Assignor to The Prest-O-Lite Co., Inc., Indianapolis, Ind. U.S. Pat. 1,185,959, June 6, 1916. Date of appl., June 24, 1915.

PLATING nickel anodes are built up from scrap anodes, by permanently uniting a number of them to a support or base by autogenous welding, so as to form a single anode.—B. N.

*Metals [copper]; Process of extracting*—— from ores. W. E. Greenawalt, Denver, Colo. U.S. Pat. 1,186,306, June 6, 1916. Date of appl., May 7, 1912.

COPPER ores are treated with an acid chloride solution which is then run off and the copper precipitated by hydrogen sulphide. The copper sulphide is separated from the regenerated acid solution and electrolysed in a sulphate electrolyte for the recovery of copper and sulphur, the latter being converted to hydrogen sulphide. Chlorine is passed through the regenerated acid solution which is then returned to the ore to extract precious metals and more copper.—T. St.

*Electrochemical amalgamator.* S. S. Rose, San Jose, Cal. U.S. Pat. 1,186,335, June 6, 1916. Date of appl., Mar. 25, 1915.

AN annular receptacle containing mercury is provided with "runways" projecting inwards from its inner and outer circumference, and rollers, carrying insulated frames, are mounted on the runways. Sweeper bars are mounted on the

frames, which are driven by gearing, and drag bars are spaced behind and connected with the sweepers. The forward edges of the drag bars are curved, and both the sweepers and drag bars move in close proximity to the surface of the mercury. Another insulated frame secured to the receptacle, and arched over the gearing, carries a roller which bears on the gearing. Wire connections from the latter frame, and from the receptacle are connected to a source of electricity.—B. N.

*Crucible furnaces and the like; Tilling*——. Alldays and Onions Pneumatic Engineering Co., Ltd., and E. W. Nicholson, Birmingham. Eng. Pat. 16,394, Nov. 20, 1915.

*Electrolytic apparatus [for production of alkali metals].* J. Pfeiffer and F. Ott, Frankfurt, Germany, Assignors to The Roessler and Hasslacher Chemical Co., New York. U.S. Pats. 1,186,936 and 1,186,937, June 13, 1916. Dates of appl., June 16 and Oct. 2, 1913.

SEE Eng. Pats. 1933 of 1913 and 10,193 of 1914; this J., 1913, 948; 1915, 909.

*Metals from tinning, galvanising, and like waste; Recovery of*——. M. E. Rothberg, Crafton, Pa., U.S.A. Eng. Pat. 100,657, Feb. 8, 1916. (Appl. No. 1803 of 1916.)

SEE U.S. Pat. 1,170,342 of 1916; this J., 1916, 364.

*Manufacture of abrasive materials.* U.S. Pat. 1,187,225. See VIII.

## XI.—ELECTRO-CHEMISTRY.

### PATENTS.

*Electrolytic apparatus.* W. E. Greenawalt, Denver, Colo. U.S. Pat. 1,186,898, June 13, 1916. Date of appl., Aug. 28, 1913.

VERTICAL cathodes and anodes are suspended alternately in the electrolyte, the anodes being completely surrounded by diaphragms, forming anode cells suspended on pivots so that they may be oscillated. Means are provided for withdrawing the electrolyte from the anode chamber without allowing it to mingle with the cathode liquor.—B. N.

*Secondary battery plates.* Electrical Power Storage Co., Ltd., London, and W. Schofield, Southend-on-Sea. Eng. Pat. 9012, June 18, 1915.

A THICK paste is formed by adding 25 parts by weight of lead oxides to a mixture of one part each of glycerin and water, or one part of glycerin, 2 parts water, and 0.5 part sulphuric acid. The paste is heated to dryness in a suitable vessel between 120° and 140° C., cooled, and finally made into a paste with a mixture of sulphuric acid and water.—B. N.

*Electrolysis.* H. R. Nelson, Elizabeth, N.J., U.S.A. Eng. Pat. 10,605, July 21, 1915. Under Int. Conv., Aug. 17, 1914.

SEE U.S. Pats. 1,149,210 and 1,149,211 of 1915; this J., 1915, 909.

*Electron-emitting cathodes.* Eng. Pat. 17,580 of 1915. See IIb.

*Apparatus for producing ultra-violet radiation.* U.S. Pat. 1,186,993. See IIb.

*Electrolysis and treatment of [cadmium or copper] sulphate liquors.* Eng. Pat. 14,273. See VII.

*Refractory materials applicable as electric resistances.* Eng. Pat. 4080. See VIII.

## XII.—FATS; OILS; WAXES.

*Palm-kernel industry; Protection of the —.*

THE following recommendations are made in the Report of the Committee on Edible and Oil-producing Nuts and Seeds (West Africa):—

(1) To impose an export-duty of 2l. per ton, or more if necessary, on palm-kernels shipped to ports outside the Empire;

(2) Continuation of the campaign for the popularisation of palm-kernel cake as a feeding-stuff;

(3) New legislation to allow the addition of the words "British-made" to the word "margarine" on the statutory wrapper for margarine;

(4) The continuation and extension of the joint researches on the oil palm, carried on by the West African Agricultural and Forestry Departments and the Imperial Institute.

The British West African Government has been instructed to put the first and fourth recommendations into action.

*Stearolic acid; Isomerides  $T_{7.8}$  and  $T_{5.6}$  of —.*

S. Posternak. *Comptes rend.*, 1916, 162, 944—946.

MELTED tarric acid (1 mol.) was treated with dry hydriodic acid until the increase in weight corresponded to two mols. of HI. The resulting brown oil was dissolved in 30% alcoholic potassium hydroxide solution, heated for 3 hours on the water-bath, the soap solution filtered from the crystals of potassium iodide and decomposed with dilute sulphuric acid. Crystals consisting of a mixture of the three isomeric stearolic acids ( $T_{7.8}$ ,  $T_{6.7}$ , and  $T_{5.6}$ ), contaminated with oily moniodo-oleic acid, were obtained. The mass was dissolved in alcohol and treated with N/1 alcoholic sodium hydroxide solution to obtain crystals of the sodium salts of the three acids. By decomposing these with sulphuric acid, and crystallising the product from alcohol, nearly pure tarric acid ( $T_{6.7}$ ) separated first. The residual acids were converted into di-iodo derivatives and dissolved in alcohol. On cooling the solution di-iodo-7,8-claidic acid (m.pt. 68° C.) separated, and from this by treatment in alcoholic solution with metallic sodium the  $T_{7.8}$  isomeride (m.pt. 49.25° C.) was obtained. The  $T_{5.6}$  isomeride was separated by eliminating the iodine from the mother liquors, dissolving the recovered acids in alcohol, and adding successive portions of N/1 alcoholic sodium hydroxide solution. Repeated recrystallisation of the fractions melting above 44° C. yielded the  $T_{5.6}$  isomeride (m.pt. 52.5° C.).—C. A. M.

*Use of castor oil for removing resin from rubber and guttapercha.* Schopper. See XIV.*Cause and prevention of rancidity in palm nut kernel cake.* Calder. See XIXa.*Croton-resin.* Boehm. See XX.

## PATENTS.

*Unsaturated materials [oils]; Process and apparatus for reducing —.* A. H. Ney, Hiasbrouck Heights, N.J., Assignor to Hydrogenated Oil Co., New York. U.S. Pat. 1,185,704, June 6, 1916. Date of appl., June 7, 1912.

THE oil, etc., in a state of fine division ("oil-fog") is brought into contact with hydrogen or a gas containing hydrogen in presence of a movable permeable catalyst, which is constantly freed from the hydrogenated oil.—C. A. M.

*Detergives and emulsive agents; Manufacture of —.*

R. Macpherson, Brondesbury, and W. E. Heys, Bushey. Eng. Pat. 8478, June 8, 1915.

PROTEINS or farinaceous substances or substances containing them are treated in the cold with solid

caustic soda or potash, with or without added fats or fatty acids, and in presence of only sufficient water to effect the reaction, whereby a practically dry detergent is obtained.—C. A. M.

## XIII.—PAINTS; PIGMENTS; VARNISHES; RESINS.

*Linseed oil; Effect of certain pigments on —.*

E. W. Boughton. U.S. Bureau of Standards. Techn. Paper, No. 71, Apr. 13, 1916, 1—16.

IN a former communication (this J., 1913, 371) it was shown that the constants of linseed oil mixed with various pigments and kept in closed cans for 2 years showed only slight changes. The remainders of the paints used in these experiments were placed in glass jars, which they partially filled, and these jars were closed and exposed to diffused light for 1 year. The oil was then extracted with ether and examined. Considerable changes had taken place in the constants of the oil except in the case of the zinc yellow, chrome yellow, and artificial graphite pigments. White lead and zinc white were the only pigments which had caused a large increase in the ash yielded by the oil (1.02 and 0.99%, respectively, as compared with 0.13% from the original oil). The oil from the white lead paint was orange-red, viscous, and had a skin on the surface. Its iodine value had fallen to 145. In other experiments white lead and zinc white were mixed with raw or boiled linseed oil, and thin films of the paints brushed over glass. After intervals of 6 hours to 8 days the films were removed and treated with a mixture of benzene (60 vols.) and 95% methyl alcohol (40 vols.), and the extract centrifuged and filtered through paper pulp. The extracted oils were red and viscous and had an acid odour. In the case of the mixture of raw oil and white lead, the iodine value of the fatty acids had fallen from 194 to 163, while the ash of the oil had increased from 0.11 to 0.85 after 6 days. The corresponding figures for the oil extracted from the film of zinc white paint were 191 and 2.17% after 8 days. The oil from the mixture of boiled oil and white lead showed:—iodine value of fatty acids 143 (original value, 182) and ash 0.82% (original oil, 0.56%) after 6 hours, while the oil from the mixture of zinc white and boiled oil showed:—iodine value 141 and ash 1.60% after 6 hours. These results indicated that there was an appreciable combination of oil and pigment on exposure of the paints to the air. On mixing white lead and zinc white respectively with linseed oil fatty acids, considerable combination occurred, the amount of zinc soap produced being about four times as much as the amount of lead soap. In experiments in which films of raw linseed oil mixed with the pigments were exposed to oxidation, white lead had a greater accelerating influence than zinc white, and the latter a greater effect than China clay on the oxidation.—C. A. M.

*Self-luminous paint.* F. H. Glew. Optical Soc. June 8, 1916. Chem. and Drug., 1916, 88, 653.

WHEN radium is mixed with a zinc sulphide, it exerts a continuous excitation on the sulphide and eventually exhausts it. The Admiralty specification for radium luminous paint is 0.4 mgm. of radium bromide per gram of zinc sulphide; the paint is also made with half this proportion of radium. At the end of a year it is probable that paint made to the Admiralty specification will have only half its original luminosity. The more radium the paint contains the shorter will be the life of the zinc sulphide. The act of mixing the paint exhausts the zinc sulphide somewhat, and it requires time for the radium to excite it to

further action. A palette-knife must not be used for mixing the paint or the crystalline structure of the zinc sulphide will be destroyed, with a corresponding loss of illuminating-power. Other substances than radium are used in paint, mesothorium more frequently. Ionium would be an ideal substance, but it is not obtainable in a pure state.

*Oleo-resinous exudation of conifera; Improved method of collecting the*—. H. Wislicenus. Chem.-Zeit., 1916, 40, 559—560.

THE ordinary method of obtaining the resinous exudation from pines (by excision and collection in open vessels) is very wasteful, since upwards of 50% of the oil of turpentine present may evaporate from the resin during its exposure to the atmosphere. An improved method consists in boring a hole into the tree and inserting the neck of a bottle into this hole; other smaller holes are bored through the outer portion of the tree and connect with the first hole, the outer ends of the smaller holes being plugged. The fluid resin, rich in turpentine (about 38%), collects in the bottle. —W. P. S.

#### PATENTS.

*Coating composition [for concrete and cement]*. C. Ellis and A. A. Wells, Montclair, N.J. U.S. Pat. 1,179,413, Apr. 18, 1916. Date of appl., Aug. 13, 1912.

A COMPOSITION for painting concrete and cement structures is made by heating Pontianak (Borneo) rubber resin (jelutong) for about four hours at 675°—700° F. (357°—371° C.) or higher, in a retort fitted with a reflux condenser, so as to decompose it with formation of acetic and similar acids (which are removed by distillation) and a neutral oily unsaponifiable resin which is readily soluble in benzene and has siccativ properties. The product is dissolved in benzene or other suitable solvent, passed through a tower filled with quicklime to remove any acids, and may then be used alone or incorporated with drying oils, dryers, or with suitable thickeners.—A. B. S.

*Finish-removing process*. C. Ellis, Montclair, N.J., Assignor to Chadeloid Chemical Co., New York. U.S. Pat. 1,185,641, June 6, 1916. Date of appl., Oct. 10, 1911.

To remove a coating of paint, varnish or other finish, the article is immersed in or treated with an organic solvent of high boiling-point (over 200° C.) previously heated to over 90°—100° C. When the temperature of the article has reached substantially that of the solvent, the article is taken out, and when the finish has been dissolved, softened or loosened, the surface is cleaned with volatile liquid.—E. W. L.

*Drying or hardening [siccativ] coatings; Process for*—. W. M. Grosvenor, Grantwood, N.J., Assignor to Wenborne-Karpen Dryer Co., Chicago, Ill. U.S. Pat. 1,186,477, June 6, 1916. Date of appl., Nov. 20, 1908.

THE coatings are subjected simultaneously to heat and to the action of a more powerful oxidising agent than air, in the presence of moisture in excess of the natural humidity.—W. F. F.

*Condensation products of phenols and formaldehyde; Process of making*—. L. H. Baekeland, Yonkers, N.Y., Assignor to General Bakelite Co., New York. U.S. Pat. 1,187,229, June 13, 1916. Date of appl., Oct. 2, 1909.

COMPACT, coherent bodies containing insoluble, infusible condensation products of phenols and formaldehyde and a basic substance, are formed by adding to a mixture of phenols and a substance

containing a mobile methylene group (formaldehyde) a basic condensing agent in excess of the proportion desired in the final product, then eliminating the undesired excess of condensing agent by adding a reagent which yields with it an insoluble compound, and hardening the mass by heat and pressure.—E. W. L.

*Reaction product of hexamethylenetetramine and phenolic bodies, and method of making same*. L. H. Baekeland, Yonkers, N.Y., Assignor to General Bakelite Co., N.Y. U.S. Pat. 1,187,230, June 13, 1916. Date of appl., Dec. 13, 1910.

PHENOLS are heated with hexamethylenetetramine, with or without the addition of water, until the water and a portion only, or the whole, of the ammonia have been expelled, and the product is hardened by the application of heat and pressure. The final product is a yellow mass somewhat resembling amber, and containing, in the one case, uncombined ammonia.—E. W. L.

*Phenolic condensation product and method of making the same*. L. H. Baekeland, Yonkers, and N. Thurlow, New York, Assignors to General Bakelite Co., N.Y. U.S. Pat. 1,187,231, June 13, 1916. Date of appl., Dec. 11, 1912.

THE condensation product is formed by the action of a phenol upon a salt (the hydrochloride) of hexamethylenetetramine, and is rendered infusible and insoluble by the application of heat.—E. W. L.

*Insoluble bodies derived from phenol alcohols; Process for making*—. L. H. Baekeland, Yonkers, N.Y., Assignor to General Bakelite Co., N.Y. U.S. Pat. 1,187,232, June 13, 1916. Date of appl., May 15, 1915.

HARD, compact, infusible bodies or moulded articles are produced by eliminating water from phenol-alcohols and hardening the anhydrides, by the action of heat and pressure, in presence of a basic condensing agent, and in presence also, if desired, of suitable filling materials.—E. W. L.

#### XIV.—INDIA-RUBBER; GUTTA-PERCHA.

*Plantation rubber of uniform quality; Preparation of*—. Arens, Gummi-Zeit., 1915, 29, 1248—1249. Chem.-Zeit., 1916, 40, Rep., 218.

THE quality of the rubber is not appreciably affected by the method of tapping the trees, but addition of water to the latex produces variations in quality and should be avoided on the plantation unless the quantity added is under strict control; in the factory, dilution of the latex with an equal volume of water is recommended, especially in the preparation of thin sheet rubber. The nature of the acid used as coagulant is of no importance so long as only the minimum quantity necessary to produce coagulation is added, but dilute acid can be distributed more uniformly in the latex than concentrated acid. The duration of the period between coagulation and working-up of the coagulum has considerable influence on the quality of the rubber. Artificial drying in vacuum dryers or similar apparatus always causes deterioration in the quality of rubber. Drying in smoke chambers, at a temperature not exceeding 55° C., gives better results than air-drying, and within certain limits, the quality is better the longer the rubber remains in the smoke chamber.—A. S.

*Rubber and gutta-percha; Use of castor oil for removing resin from*—. T. Schopper, Gummi-Zeit., 1916, 30, 601. Z. angew. Chem., 1916, 29, Ref., 295.

THE purification of raw rubber by extraction with

castor oil possesses the following advantages. All resinous constituents are removed and the water present in the rubber is evaporated, and hence the further purification of the rubber is facilitated and less alcohol is required. Only a short extraction with castor oil is required. The solution of rubber resins in castor oil can be used in the manufacture of soaps.—A.S.

*Rubber; The effect of vacuum drying crêpe* —  
B. J. Eaton. Agr. Bull. Fed. Malay States, 1916, 4, 219—221.

FROM the results of a long series of vulcanisation tests with thin crêpe dried at ordinary temperature in a drying room, another portion of the above dried in a Passburg vacuum drier, and a portion of the latter re-machined after removal from the drier, as is usual on the estates, the author concludes that neither the rate of cure nor the physical properties are affected by the vacuum drying process.

—E. W. L.

*Rubber; Action of alkalis and acids on* —  
B. J. Eaton. Agr. Bull. Fed. Malay States, 1916, 4, 162—167. (Cf. Martin, this J., 1915, 725.)

SAMPLES of fast- and slow-curing crêpe rubber were soaked in dilute solutions of sodium and potassium hydroxides, and the re-crêped samples were vulcanised. The acceleration of the rate of cure was about the same for soda as for potash, and for slow-curing as for fast-curing rubbers. Slow-curing rubber which had been soaked in alkali, and neutralised on the following day with acetic acid, was found still to be slow-curing, but when neutralisation was not carried out until 10 days after soaking, the rubber cured more rapidly than the control. Rubber soaked in alkali and re-crêped became very tacky and soft on keeping. The use of mineral acids and of potash alum in coagulation tends to retard the cure, more especially when even slight excess over the minimum quantity necessary is used. The greatest care should therefore be taken to keep conditions constant when coagulating with sulphuric instead of acetic acid.—E. W. L.

#### PATENTS.

*Rubber latex; Apparatus for coagulating and drying* — S. Milne, Edinburgh. Eng. Pat. 9039, June 19, 1915.

A CYLINDER, about 10 ft. diameter and 12 ft. long, is provided on its surface with blade- or plate-like flanges, 1 ft. 6 in. deep or more, arranged either parallel to one another, and at right angles to the axis of the cylinder, 2 inches apart; or spirally round the cylinder; or inclined to the axis; or in zig-zag fashion. As the cylinder revolves the blades dip into an open steam-jacketed pan containing heated latex, a thin film of latex is carried round on the blades, and the drying of this is further facilitated by passing hot air through the cylinder housing. A large surface of evaporation is thus provided in a small space.—E. W. L.

*Rubber; Manufacture of — and apparatus therefor.* C. A. Icken and St. V. B. Down, Singapore. Eng. Pat. 8487, June 8, 1915.

LATEX is coagulated by adding to it, in the form of liquid, liquid spray, or vapour, a mixture of alcohol—either absolute alcohol, or methylated spirit, or normal or iso-propyl alcohol—and a hydrocarbon solvent, such as petroleum spirit (b.pt. 40°—150° C.) or coal-tar naphtha (b.pt. 80°—140° C.) or motor spirit. In the case of *Hevea Brasiliensis* latex the proportions recommended are:—methylated spirit, 5% of the weight of latex; petroleum spirit, 10% of the weight of rubber in the latex. Coagulation occurs rapidly,

and the rubber is then removed, pressed, and dried. The methylated spirit can be recovered, but the petroleum spirit is allowed to remain and evaporate slowly from the rubber. In crêping the bulk of the resins dissolved in the petroleum spirit, and proteins will be eliminated by pressure. The temperature should not be allowed to rise above 90° F. (32° C.).—E. W. L.

*Caoutchouc; Method of producing synthetic* —  
E. Gottschalk, Newark, N.J. U.S. Pat. 1,185,654, June 6, 1916. Date of appl., May 17, 1911.

PINENE is "cracked" by passage in the form of vapour, through a tube heated to 300°—350° C. (572°—662° F.), and the emergent vapour is cooled quickly. The hydrocarbons thus formed are distilled, and the distillate, either alone or in presence of an acid reagent, is heated in a closed vessel, thereby creating pressure. The temperature is then kept constant, while the pressure falls until it reaches a point where it remains substantially constant. At this point any volatile matter is distilled-off, and the residue oxidised.—E. W. L.

*Coating composition for concrete and cement.*  
U.S. Pat. 1,179,413. See XIII.

#### XV.—LEATHER; BONE; HORN; GLUE.

*Adsorption [of organic acids by hide powder].* V. Kubelka. Collegium, 1915, 389—408. J. Chem. Soc., 1916, 110, ii., 297.

AQUEOUS solutions of formic, acetic, propionic, and butyric acids were shaken at a temperature of 19°—21° C. with a weighed quantity of standardised non-chromed hide powder, and the changes in concentration of the acid solution determined.

The results obtained show that the removal of the acids from aqueous solution takes place very rapidly and that a condition of reversible equilibrium is attained in each case. The relation between the quantity of acid removed by a given weight of hide substance and the concentration of the aqueous solution in equilibrium may be represented by the well-known adsorption formula. For the three higher aliphatic acids the adsorption constant  $\beta$  is proportional to the ionisation constant of the acid.

*Influence of pine resin and tannin on the nitrogen economy and on the physical properties of the soil.*  
Koch and Oelsner. See XVI.

#### PATENTS.

*Tanning; Process of* — H. Morin. St. Denis. France. Eng. Pat. 100,163, Mar. 14, 1916.  
Under Int. Conv., Oct. 22, 1914. (Appl. No. 3802 of 1916.)

SKINS, after thorough rinsing, are soaked in a solution containing from 2½% to 10% of sodium or potassium silicate, and afterwards treated with acetic or some other acid to precipitate silica on the hide fibre. The leather produced is white, supple, and unaffected by boiling water.—F. C. T.

*Impregnation of leather or textile driving belts or the like.* O. Heublein, Frankfurt. Ger. Pat. 291,461, Jan. 10, 1915.

THE belts are impregnated with a solution, liquid at the ordinary temperature, of wool fat, pitch, or the like, in a volatile solvent. Suitable solvents are chloro-derivatives of aliphatic hydrocarbons, petroleum, ketones, aromatic hydrocarbons, oil of turpentine, chlorohydrins, or mixtures of these substances.—A. S.

[Glue] adhesive, and process of making same. C. H. Campbell, Chicago, Ill., Assignor to American Glue Co., Boston, Mass. U.S. Pat. 1,184,071, May 23, 1916. Date of appl., Oct. 12, 1912.

A SMALL quantity of a soluble nitrate is added to a solution of glue, which is then heated for a short time to about 120° C. After drying, the glue is soluble in water at the ordinary temperature.—F. C. T.

Leather substitute; Process for the manufacture of a material suitable for use as a ——. J. Chylik, Krizenau, Austria. Eng. Pat. 8821, June 15, 1915.

ROBIN (0.2 kilo.) is heated with linseed oil varnish (0.28 kilo.) until a viscous solution is formed. This is cooled, and milk curd (1 kilo.) is added, the whole being worked up to a stiff paste; slaked lime (0.50 kilo.) is then added so as to produce a paste suitable for spreading. Canvas or other fabric may now be coated or impregnated with this paste, and built up to the required thickness. The product is dried, and then softened in water, when it can be pressed into sheets or plates. The paste may also be mixed with finely divided leather waste, and rolled or pressed into sheets.—E. W. L.

Gelatinising substances; Treatment of ——. Aktienges. für Chemische Produkte vorm. H. Scheidemann, Berlin, Assignees of P. Askenasy, Karlsruhe, Germany. Eng. Pat. 100,392, Mar. 30, 1916. Under Int. Conv., May 3, 1915. Addition to Eng. Pat. 15,365 of 1915.

GELATIN globules, formed by the cooling of drops of a hot solution of gelatin, may be thoroughly cooled and prevented from adhering together by using a cooling liquid of such specific gravity that the globules do not sink in it until they are nearly solid, and too hard on the surface to permit adhesion.—F. C. T.

Tanning substances and method of preparing the same. A. Römer, Stuttgart, Assignor to Deutsch-Koloniale Gerb- u. Farbstoff-Ges.m.b.H., Karlsruhe, Germany. U.S. Pat. 1,186,500, June 6, 1916. Date of appl., Jan. 24, 1916.

SEE Fr. Pat. 471,924 of 1914; this J., 1915, 438.

Process for dyeing artificial leather. U.S. Pat. 1,186,052. See VI.

## XVI.—SOILS; FERTILISERS.

Sulphur in moorland soils injurious to plant growth and subterranean structures; Nature of the ——. W. Thörner. Z. angew. Chem., 1916, 29, 233—236.

THE so-called reactive sulphur which is deleterious to both plant growth and the mortar or cement of underground foundations, etc., occurs not only as pyrites, but also in the free state and in organic combination. Its destructive action is ascribed to the production of sulphuric acid by atmospheric oxidation in presence of moisture. Finely divided sulphur mixed with moist sand or peat on a filter underwent slow oxidation as the water evaporated, and similar conditions may be assumed to exist in peaty land containing sulphur, on exposure to the atmosphere. An energetic oxidation of finely divided sulphur in aqueous suspension was observed during electrolysis of the water.—G. F. M.

Molasses; Utilisation of (cane) — as a manure. L. de Wall. Intern. Sugar J., 1916, 18, 267—272.

A SERIES of plots in Java was treated with sulphate of ammonia. Some of these in addition received: (1) a solution of cane molasses; (2) a solution of

sugar of the same sucrose content as the molasses; and (3) the nitrogen, and (4) the nitrogen and potash equivalent to the amounts present in the molasses added. In the case of the molasses and the sugar plots the increased tonnage of cane per acre over that found when using sulphate of ammonia alone was 10—11 and 6.5 respectively; whereas in the extra nitrogen and extra nitrogen and potash plots it was 2½—3½ and 3—4 tons. Notwithstanding, however, these increased yields of cane caused by the presence of sugar, the available sugar of the cane was markedly decreased. Application of the molasses was made in these experiments in the form of a solution, which would immediately drain to the lower strata of the soil. Probably a more advantageous procedure would have been to use "solidified molasses."—J. P. O.

Zeolites; Chemical and physical properties of artificial ——. A. von Sigmund. Kir. Magyar Termész. társulat, Budapest, Feb. 29, 1916. Chem.-Zeit., 1916, 40, 519—520.

EXPERIMENTS were made with artificial sodium-zeolites containing widely varying molecular proportions of silica, alumina, and soda, which were converted into calcium-zeolites by treatment with 26% calcium chloride solution. The calcium zeolites obtained were of four kinds and possessed the following molecular compositions:—

- (1)  $3\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO} + 3\text{H}_2\text{O}$ ;
- (2)  $7\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{CaO} + 6\text{H}_2\text{O}$ ;
- (3)  $9\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{CaO} + 8\text{H}_2\text{O}$ ;
- (4)  $23\text{SiO}_2 \cdot 4\text{Al}_2\text{O}_3 \cdot 4\text{CaO} + 20\text{H}_2\text{O} + \text{CaSiO}_3$ .

The reaction is a true chemical reaction and does not result in the formation of gel complexes; there is evidence of crystalline structure in the products. The sodium-zeolites are slimy products whilst the calcium-zeolites are granular. This corresponds with the fact that soils containing natural sodium-zeolites in quantity have poor physical properties which can be improved by treatment with calcium salts. There is thus a close connection between the physical properties of a soil and the chemical properties of the zeolites which are present.—J. H. J.

Soil acidity; Cause and nature of — with special regard to colloids and adsorption. E. Truog. J. Phys. Chem., 1916, 20, 457—484.

THE production of acidity or alkalinity when certain neutral solutions come in contact with certain solids is probably due to chemical action and not to selective adsorption of ions. Cameron's contention that the acid reaction towards litmus of washed absorbent cotton (and inferentially of certain soils) is due to adsorption of cations, is untenable, since such cotton has been found to contain an insoluble fatty acid (perhaps margaric acid), which would not be removed completely by the preliminary washings with alkali and acid. When the cotton is brought into a neutral salt solution, the salt reacts with the fatty acid, some cations are removed, and an equivalent amount of soluble acid is liberated. Similarly, the reputed selective adsorption of ions by charcoal is accounted for by chemical actions between impurities contained in it and the dissolved salt. Assuming selective adsorption, the vastly greater adsorptive power of soils would still need explanation. Arguments are also adduced to prove that soil acidity is not the result of selective ion-adsorption by colloids or by finely divided solids; and it is shown experimentally that under suitable conditions, the reactions causing soil acidity proceed according to chemical laws. The acidity in well aerated soils, in particular in cultivated upland soils, is due to hydrolysis of silicates, of which the bases are removed by plants and by soil water, and the silica and acid silicates left



behind. The weathering process in soils can be reproduced by treating powdered basalt, granite, felspar, etc., with carbonated water and filtering: the residues are acid to litmus. In dry regions, the soluble salts accumulate and cause alkalinity. In these soils, organic acids derived from plant residues are of little importance: they may be formed, but are quickly transformed. In badly aerated soils, *e.g.*, in peat soils, the plant remains are decomposed much more slowly; instead of being oxidised to carbon dioxide, much of the carbon remains in the soil in organic combination as the so-called humic acids, and eventually is transformed into coal. The latent acidity of a soil (see this J., 1916, 699) may be largely due to kaolinite and similar compounds, or to free quartz; and the results of the determinations of active and latent acidity show that the amounts of different hydroxides that react with the insoluble acids, are approximately chemically equivalent. The fact that acid soils do not take up equivalent amounts of different bases from salt solutions possessing a common ion, is not opposed to the hypothesis that soil acidity is due to the presence of free acids, for the reactions involved would be much influenced by secondary reactions. By using small quantities of finely powdered soil and large volumes of salt solutions, and minimising the time of contact, the effect of such side reactions can be practically annulled; and determinations of soil acidity, under these conditions, give results which are best explained on the assumption of the existence of free acids. Further, the adsorption hypothesis would lead to the conclusion that the acidity of a soil would increase if the particles were ground to an impalpable powder: experiments showed a slight decrease.—E. H. T.

*Bacterium; A hydrogen-oxidising* — from Indian swamp rice soils. W. H. Harrison and P. A. Subramania Aiyer. Mem. Dept. Agric. India, Chem. Series, 1916, 4, 135—148.

CRUDE cultures of the bacterium found in the soil-film of swamp rice land (this J., 1913, 1165, and 1915, 190) developed very poorly in Kaserer's solution ( $K_2HPO_4$ , 0.05%,  $MgSO_4$ , 0.02%,  $NH_4Cl$  0.1%,  $NaHCO_3$ , 0.05%,  $FeCl_3$ , trace), and when plated out on silica jelly, or on washed agar media containing the salts forming Kaserer's solution, and incubated in an atmosphere of mixed carbon dioxide, methane, oxygen, and hydrogen, did not oxidise the hydrogen except in one instance. In this case the microscope revealed two species of bacteria, a non-motile organism and a pseudomonas. Inoculation of this mixed culture into Kaserer's solution containing 0.1% of sodium asparaginate, caused a greatly increased oxidation of hydrogen. By repeated plating and re-plating on mineral agar containing the asparaginate, a pure culture of the oxidising non-motile bacterium was isolated, which was not identical with Kaserer's organism, *B. pantotrophus*. It is about 1–4  $\mu$  long and 0.5  $\mu$  broad, stains readily with aqueous stains, has no flagellæ and is non-spore-forming. It gives a white gelatin stab culture, and does not reduce nitrates or ferment sugars. Practically inactive under autotrophic conditions, it oxidises hydrogen in symbiosis with the motile bacterium mentioned above. In presence of sodium asparaginate, peptone, or nitroase (optimum amounts, 0.01–0.03%) oxidation takes place readily, but excess of such organic matter inhibits the action. The presence of the motile organism promotes oxidation when the organic substances are also present, and only in this case was complete oxidation observed. The organism utilises ammonia and nitrates in presence of dextrose, but under these circumstances no oxidation of hydrogen takes place.—E. H. T.

*Carbon and nitrogen changes in soil variously treated: soil treated with calcium carbonate, ammonium sulphate, and sodium nitrate.* R. S. Potter and R. S. Snyder. Soil Science, 1916, 1, 76–94. J. Chem. Soc., 1916, 110, 1, 459–460.

THE soil employed was a silt loam containing 1.35% of carbon and 0.1137% of nitrogen; its lime requirement was 600 lb. per acre according to the Veitch method (this J., 1904, 762). The amounts of ammonia and carbon dioxide given off by the soils, both alone and with addition of ammonium sulphate and sodium nitrate respectively, without and with calcium carbonate, were estimated by passing air over the soil contained in pots under bell-jars, and then successively through standard acid and 5% potassium hydroxide. Considerable amounts of carbon dioxide were given off during the first two days from the soil alone and from the soil with sodium nitrate; with ammonium sulphate the amount was much higher; and with calcium carbonate very much higher, whether employed alone or in conjunction with the nitrogenous manures. The production of carbon dioxide rapidly fell, but remained highest in the pots which received calcium carbonate. As regards the origin of the carbon dioxide, it is shown that in this experiment addition of calcium carbonate diminished its production from the organic matter; in another experiment the organic matter yielded more carbon dioxide when calcium carbonate was added than without. The loss of ammonia amounted to about 0.3 lb. per acre in twelve weeks, and was only higher (about ten times) in the pots which received both calcium carbonate and ammonium sulphate. The losses of total nitrogen were generally less and the gains greater when calcium carbonate was added than without it.

*Pine resin and tannin; Influence of — on the nitrogen economy and on the physical properties of the soil.* A. Koch and A. Oelsner. Centr. Bakt. Par., 1916, ii., 45, 107–118. J. Chem. Soc., 1916, 110, i., 454.

IN soil to which 5% of colophony and 0.025% of nitrogen as nitrate were added, the whole of the nitrate was denitrified by bacteria, which utilised the colophony as source of energy, in four weeks. The total nitrogen of the soil was only slightly diminished, so that the nitrate was utilised as source of nitrogen without liberation of free nitrogen. In an experiment in which colophony was substituted for citric acid in a Giltay solution, there was a slight reduction of nitrate to nitrite in a few days. The reduction was more vigorous in a Raulin solution, with colophony instead of sugar, owing probably to the solvent action of the potassium carbonate on the resin. It is possible that nitrification is hindered by the presence of resin constituents dissolved by alkali salts. Tannin is readily assimilated by mould fungi, and the increased growth of the fungi gives rise to a temporary loss of nitrogen present in the forms of ammonium salts and nitrates, which explains the low amounts of nitrates found in soils containing tannin. No oxalic acid is produced by *Aspergillus niger* from tannin. Addition of tannin to soils results in the production of a dark colour not due to iron. The power of retaining water is increased by addition of tannin to soils. Large additions of tannin render soils hard like stone, owing perhaps to the precipitation of colloids.

*Calcium cyanamide; Effect of varying amounts of admixed water upon the decomposition of crude —, and the formation of diacyandiamide.* G. Hager and J. Kern. Z. angew. Chem., 1916, 29, 221–223.

QUANTITIES of crude calcium cyanamide of 100

grms. each were treated separately with 5, 10, 15, 25, and 50 grms. of water, and enclosed in air-tight glass vessels. After 5 and 7 months the material was analysed. The fertiliser used contained: total nitrogen 18.62%, of which 17.73 was water-soluble, cyanamide-nitrogen 16.75%, nitrogen as dicyandiamide 0.50%, as ammonia 0.24%, and as "urea" nitrogen (*i.e.*, the element left in the filtrate after precipitation of the dicyandiamide) 0.48%. Seven months' storage without added water caused no perceptible change: with 5 and 10 grms. of water, the changes were very small, the dicyandiamide nitrogen rising to 0.61 and 0.87% respectively. The presence of 15 grms. of water produced more change; the dicyandiamide nitrogen rose to 1.13%, the urea-nitrogen to 0.71%, the cyanamide nitrogen fell to 13.61%, and the ammonia nitrogen to 0.14%. Very little change took place in the first ten days when 25 grms. of water was added, but after 7 months, 2.58% of dicyandiamide was found. With 50 grms. of water, profound changes took place and the material set to a hard stone-like mass; after 2½ months and 7 months, the dicyandiamide nitrogen rose to 7.51 and 9.17% respectively, the cyanamide nitrogen falling to 2.81 and 0.28% respectively in the same periods. The analyses were performed by Caro's method (compare this J., 1916, 647). Calcium cyanamide should not be stored after it has become wet, but may be used immediately; the use of water to produce it in a granulated form is not likely to succeed.—E. H. T.

*Phosphoric acid; Determination of*—by the *citro-uranium method*. D. Crispo and R. W. Tuining. Landw. Versuchs-Stat., 1916, 88, 131—141. J. Chem. Soc., 1916, 110, ii., 342.

THE citrate-soluble phosphoric acid in phosphatic fertilisers may be estimated by precipitating the phosphoric acid as ammonium magnesium phosphate under the conditions described by Popp (this J., 1912, 831), dissolving this precipitate in hot acetic acid, and titrating the solution with standardised uranium acetate solution, using potassium ferrocyanide as the indicator. For the estimation of total phosphoric acid in fertilisers containing much silica, the interfering action of the latter may be eliminated by boiling 10 grms. of the sample with 5 grms. of ferrous sulphate and filtering the mixture. Results of numerous estimations of phosphoric acid in a variety of fertilisers are recorded, showing that the results obtained by the method are trustworthy.

*Arsenic; Stimulating influence of*—upon the *nitrogen-fixing organisms of the soil*. J. E. Greaves. J. Agric. Res., 1916, 6, 389—416. (See this J., 1915, 808.)

THE influence of arsenic compounds upon soil fertility is complicated by the fact that the anion and cation of the salt may act in co-operation or antagonistically. Thus the good effect of lead arsenate is due to both lead and arsenate ions, and the injurious nature of Paris green is the result of the toxic action of the copper preponderating over the beneficial action of the arsenic. Arsenic cannot take the place of phosphorus as a source of energy for nitrogen-fixing organisms, but in some unknown manner it renders available the phosphorus that is present in insoluble forms; it also stimulates the cellulose ferments which in their turn promote the activity of these organisms. The nitrogen-fixing powers of soil extract, unfiltered or filtered, and of soil which has been dried for some time, are but little affected by arsenic, indicating that this stimulant acts mainly by removing a thermolabile constituent of the soil.—E. H. T.

*Fungicidal properties of certain spray fluids*. Eyre and Salmon. See XIXb.

#### PATENTS.

*Phosphoric acid; Enrichment of minerals containing*—. A. Frank, Charlottenburg. Ger. Pat. 292,090, Nov. 1, 1914.

PHOSPHATIC minerals containing calcium carbonate are calcined to convert the latter into quicklime, and this is removed in the form of oxychloride by treatment with calcium chloride solution. Basic slag may be treated directly with calcium chloride solution to remove the free lime. By treating the calcium oxychloride solution with carbon dioxide or gases containing it, calcium carbonate is precipitated and calcium chloride regenerated.—A. S.

*Superphosphate; Production of dry disintegrated*—. H. Hilbert, Neuss. Ger. Pat. 292,173, June 12, 1915.

THE fluid mixture of raw phosphate and sulphuric acid is heated by direct contact with fire-gases flowing in the same or in the opposite direction, and is at the same time continuously agitated. For example it may be passed through a series of superposed chambers, each provided with a stirrer, and traversed by fire gases. Provided the mass is kept well stirred and the duration of heating is not prolonged, a temperature of 300° C. may be used without risk of formation of metaphosphate or reversion of the superphosphate, and under these conditions the mass sets very quickly to a finely-divided product.—A. S.

*Fertiliser and method of preparing same*. W. S. Allan, Freeport, and H. H. and J. W. Sturgis, Standish, Maine. U.S. Pat. 1,178,119, Apr. 4, 1916. Date of appl., Nov. 13, 1914.

"MUSCLE mud," a shell-fish formation found in deposits on the sea coast and containing any or all of the elements, nitrogen, phosphorus, calcium, is drained, dried in heated ovens or drying cylinders, ground, and then mixed with a fertilising material, *e.g.*, a potassium mineral.—E. H. T.

*Fertilisers containing ammonium chloride, or pure ammonium chloride; Manufacture of*—. H. Precht, Hanover. Ger. Pat. 292,174, Mar. 23, 1915.

AMMONIUM-MAGNESIUM chloride, obtained by the action of ammonia on magnesium chloride solution, is dissolved in a small quantity of hot water, so that on cooling, decomposition occurs and ammonium chloride crystallises out, the magnesium chloride remaining in the mother liquor together with undecomposed double salt. The solution is evaporated and the residue again treated with hot water to decompose the double salt. Dilute aqueous alcohol may be used in place of water, and instead of dissolving the double salt it may be decomposed by stirring it with a quantity of cold water or aqueous alcohol insufficient to dissolve it completely.—A. S.

*Fertiliser from the waste liquor from potash works; Manufacture of a*—. Kaliwerke Grossherzog von Sachsen A.-G., Dietlas, and K. Hepke, Dorndorf. Ger. Pat. 292,209, Jan. 29, 1915.

THE liquor is treated with gaseous ammonia or gases containing it, for example in absorption towers, in order to convert the dissolved magnesium chloride into ammonium chloride, suitable for use as a fertiliser, and magnesium.—A. S.

*Lime-nitrogen [crude calcium cyanamide]; Improving the fertilising action of*—. A. Stutzer, Königsberg, Assignor to Bayerische Stickstoff-Werke A.-G., Berlin, Germany. U.S. Pat. 1,185,731, June 6, 1916. Date of appl., Sept. 12, 1911. SEE Ger. Pat. 242,522 of 1910; this J., 1912, 293.

## XVII.—SUGARS; STARCHES; GUMS.

*Sucrose; Determination of*—in cane products by direct polarisation after the destruction of the reducing sugars. C. Muller. Intern. Sugar J., 1916, 18, 274—275.

IN place of the use of alkali hydroxides and hydrogen peroxide, recommended by Lemeland (this J., 1910, 1220) and Vollant (this J., 1911, 1329) for the destruction of the reducing sugars previous to the determination of sucrose in cane molasses and similar products by direct polarisation, the author uses a solution containing 25 grms. of Rochelle salt and 32 grms. of sodium hydroxide in 400 c.c. of water, in which is dissolved 11 grms. of bismuth subnitrate, the mixture being made up to 500 c.c. 50 c.c. of a 40% solution of the sample contained in a 300 c.c. flask is heated with 15 c.c. of the reagent (sufficient for the destruction of 3 grms. of reducing sugars) in a boiling water-bath for 15 minutes. The liquid is then cooled, 150 c.c. of water and 60 c.c. of basic lead acetate (36° B., sp. gr. 1.33) added, the volume made up to 300 c.c., and the liquid mixed and filtered. 100 c.c. of the filtrate is treated with 5 c.c. of acetic acid, made up to 110 c.c., treated with 2 grms. of decolorising carbon, mixed, filtered, and polarised in a 400 mm. tube. Rapid and certain results, corroborating those found by double polarisation using sulphurous acid, are claimed to be obtained, and the procedure is stated to be particularly applicable to routine work in cane sugar factories.—J. P. O.

*Lead [in sugar solutions]; Determination of*—as sulphite. H. Pellet. Ann. Chim. Analyt., 1916, 21, 114—116.

THE determination of lead as sulphite (see this J., 1915, 925) was recommended by the author in 1913 (Sucrerie Belge, and Bull. l'Assoc. Chim. Sucri., 19, 362). The method gives very accurate results with the lead left in solutions of beet and cane sugar molasses after treatment with basic lead acetate. Lead sulphite is less soluble than the carbonate, particularly in presence of sugar and of the organic substances in molasses. The complete removal of lead from sugar solutions destined to be inverted with invertase, is most satisfactorily accomplished by precipitating it with an excess of sulphurous acid.—E. H. T.

*Starch; Influence of various salts on the liquefaction of*—B. Viswanath, T. L. Row, and P. A. R. Ayyangar. Mem. Dept. Agric. India, Chem. Series, Vol. IV., No. 5, 160—163.

THE authors studied the relative influence of various compounds at N/10 concentration on the rate of liquefaction of rice starch at 70° C. One grm. of starch in 50 c.c. of the liquid under investigation, was shaken continuously for 1 hour at 70° C., then cooled, treated with 15 c.c. of malt extract and kept for 2 hours at 30° C. Warth and Darabsett (this J., 1914, 433) having previously shown that at this temperature malt extract attacks only liquefied starch. The liquid was then made up to 100 c.c. and filtered with kaolin, and 50 c.c. of the filtrate was hydrolysed with hydrochloric acid and the dextrose formed was determined and calculated back to starch. The results showed that 44.91% of the starch was liquefied by distilled water alone, and the following percentages in presence of the substances indicated, at N/10 concentration:—KOH, 67.51%; Na<sub>2</sub>CO<sub>3</sub>, 26.62%; CaCO<sub>3</sub> (N/10 suspension), 25.04%; HCl, 23.00%; Na<sub>2</sub>SO<sub>4</sub>, 22.06%; MgSO<sub>4</sub>, 20.40%; NaCl, 19.00%; MgCl<sub>2</sub>, 17.14%; CaCl<sub>2</sub>, 13.50%.—J. H. L.

*Sugar formation in the sulphite-cellulose process.* Oman. See V.

*Utilisation of cane molasses as manure.* De Wall. See XVI.

*Use of cane sugar as adjunct and its inversion during the production of beer.* Schönfeld. See XVIII.

*Determination of gum in official syrups.* Luce. See XX.

*Biochemical synthesis of a galactobiose.* Bourquelet and Aubry. See XX.

## PATENTS.

*Starch from corn [maize]; Process for utilising waste products from the manufacture of*—W. X. Sage, Keokuk, Iowa. U.S. Pat. 1,187,392. June 13, 1916. Date of appl., Apr. 30, 1915.

THE soluble products in the waste liquors from the manufacture of maize starch are precipitated by agitating the liquors with lime, transferring to a settling tank, drawing off the supernatant liquor, forcing the sediment into a press, and drying the pressed product.—J. F. B.

*Starch; Apparatus for drying*—J. J. Merrill. Chicago, Ill., Assignor to Corn Products Refining Co. U.S. Pat. 1,183,097, May 16, 1916. Date of appl., Oct. 12, 1914.

THE starch is passed through a drying tunnel upon a truck, which runs on rails. The upper part of the truck is divided into narrow, vertical, longitudinal compartments, having sides and bottom of foraminous material and open at the top. The compartments are spaced apart to allow the air to circulate between them. When the starch is dry, the truck is withdrawn from the tunnel and inverted to discharge its contents.—W. H. C.

*Process and apparatus for revivifying or decarbonising bone-black or other filtering media.* U.S. Pats. 1,184,397 and 1,184,398. See I.

*Filler for liquids, especially for sugar juices.* Ger. Pat. 291,519. See I.

*Centrifugal machine [for drying sugar]; Automatic*—F. Villareal, Cruces, Cuba. U.S. Pat. 1,187,205, June 13, 1916. Date of appl., Oct. 1, 1914.

*"Depulverisation" of starch and the like. Material for use in brewing.* U.S. Pats. 1,186,893 and 1,186,894. See XVIII.

## XVIII.—FERMENTATION INDUSTRIES.

*Beer; Use of cane sugar as adjunct, and its inversion during the production of*—F. Schönfeld. Woch. Brau., 1916, 33, 9—11.

A REDUCTION of 40% in the amount of malt available for brewing in Germany has led to the use of cane sugar as adjunct, this being permitted on condition that the primary fermentation is carried out with top-fermentation yeast. (Cane sugar added to wort is not inverted by one hour's boiling of the wort, but if added just before or after the primary fermentation it is completely inverted in 1 or 2 days at 20° C. and more slowly at cellar temperature (cp. Baker and Hulston this J., 1914, 562). If added to beer shortly before pasteurisation it is sometimes completely hydrolysed before the operation is concluded, especially when the rise of temperature is slow, but if any sucrose remains after pasteurisation its rate of inversion is much slower than in the pasteurised beer. The author considers that if using cane sugar for German beers the addition of the sugar without prior inversion is not likely

o weaken the yeast, since the invertase acts outside the cell.—J. H. L.

*Hops; Influence of — on the protein-content, foam-retaining power, and stability of beer.* R. Heusz. Z. ges. Brauw., 1916, 39, 49—52.

In experiments in which 5.5 grms. of hops was boiled for 1 hour in about 1 litre of water, the amount of nitrogen (calculated as protein) extracted was only 0.369% of the dry substance of the hops, and only about  $\frac{1}{10}$  of this was precipitable by phosphotungstic acid. Further experiments indicated that the precipitation of nitrogenous matters from wort during boiling is not increased by addition of a hop-extract. The foam-holding power of a mixture of hop-extract and malt-extract was found to be far greater than that of either extract alone.—J. H. L.

*Fermentation; Mechanism of alcoholic —.* A. Fernbach. J. Inst. Brew., 1916, 22, 354—367.

THE author has previously shown that when fermentation is conducted in presence of calcium carbonate, relatively large quantities of calcium pyruvate accumulate in solution, thus confirming the view that pyruvic acid is an intermediate product of fermentation (this J., 1914, 97, 707). The quantity of acids formed, as estimated from the amount of lime dissolved at various stages of fermentation, increases approximately in proportion to the amount of sugar decomposed, and far exceeds the limit possible in absence of calcium carbonate. The total weight of salts precipitable by alcohol, obtained by the author in fermentation with yeasts, varied between 7 and 25% of the sugar, and consisted mainly of calcium pyruvate. The amount of free pyruvic acid actually isolated did not in any case exceed 5% of the sugar, owing to the tendency of the free acid to condense forming a lactone from which pyrotartaric acid is produced by elimination of carbon dioxide. This lactone may possibly play a part in the formation of succinic acid during fermentation. In fermentations conducted in presence of calcium carbonate the amount of pyruvic acid present (estimated by absorption of iodine in presence of alkali) increases until practically all the sugar is decomposed, and afterwards diminishes, for even in the form of calcium salt it is slowly decomposed by the yeast. The products of the decomposition of pyruvic acid by yeast are carbon dioxide and acetaldehyde, and the author considers that the latter is converted into alcohol by the reducing action of the yeast. The salts formed during fermentation in presence of calcium carbonate include calcium lactate, the lactic acid being formed doubtless by reduction of pyruvic acid.—J. H. L.

*Wine; Rapid method for the determination of the sulphate-content of —.* J. Pritzker. Chem.-Zeit., 1916, 40, 499—501.

For approximate determinations, 8 c.c. of wine, or a smaller quantity diluted to 8 c.c. with water, is mixed with 1 c.c. of a 10% solution of barium chloride containing hydrochloric acid, and centrifuged for 3 mins. at about 1400 revs. per min. in a tube of which the closed end is drawn out to form a narrow, graduated extension. The amount of sulphate is estimated from the volume occupied by the precipitate. When greater accuracy is required, 10 c.c. of wine may be titrated with standard barium chloride solution (14 grms.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and 50 c.c. concentrated HCl per litre; 1 c.c. corresponds to 1 gm. of  $\text{K}_2\text{SO}_4$  per litre of wine) in a centrifuge tube such as a Schmid's albuminometer. The tube is spun for 1 min. after addition of slightly less than the required amount of barium chloride (as found by the foregoing test), and again after addition of successive portions

of 0.1 c.c., so long as a drop of the barium chloride solution produces a precipitate in the supernatant liquid. The second method was found to give results in close agreement with the conductivity method of Dutoit and Duboux (this J., 1908, 871, 912), which the author considers accurate but troublesome to operate without considerable experience (cp. Bruno and D'Auzay, this J., 1912, 506, 742).—J. H. L.

*Liqueurs; Determination of essential oils [essences] in —.* X. Rocques. Ann. Falsif., 1916, 9, 127—134.

A COMMISSION appointed to investigate the methods for determining the total quantity of essential oils in various liqueurs reports that the iodine method (see Ronnet, this J., 1916, 613) yielded accurate results only in the case of liqueurs flavoured with aniseed or caraway (kummel) oils, the iodine values of these two oils being 1.45 and 2.40, respectively. In the case of all other liqueurs (Benedictine, Chartreuse, Curaçao, mint, orange bitters, etc.) the gravimetric method described by Muttelet (this J., 1916, 432, 613) should be employed. It was found that well-known brands of liqueurs frequently contained more than 0.5 gm. of essential oil per litre, the maximum limit fixed by a recent French law; in Curaçao liqueur the quantity exceeded 2 grms. per litre. Vermouth did not contain any appreciable quantity of essential oil.—W. P. S.

*Methane fermentation of ethyl alcohol.* V. L. Omeliansky. Ann. Inst. Pasteur, 1916, 30, 56—60. J. Chem. Soc., 1916, 110, i, 453—454.

AQUEOUS solutions of ethyl alcohol (1%) containing, in addition, only mineral matter in amounts necessary as bacterial food, have been submitted to anaerobic fermentation by inoculation with faecal matter from a rabbit which had previously received alcohol for a fortnight. The gas collected consisted of carbon dioxide, 11.5%; methane, 87.4%; and hydrogen, 1.1%. The solid matter collected at the bottom of the liquid was used to inoculate another solution, the gas this time consisting of carbon dioxide, 12%, and methane, 88%. Fermentation in each case continued until the whole of the alcohol was decomposed, and the bacteria persisted through a series of generations for more than a year. The bacteria were examined microscopically, and presented the forms of very slender, moderately long rods, slightly bent and without spores.

*Urease content of certain beans, with special reference to the jack bean.* J. C. Mater and E. K. Marshall, jun. J. Biol. Chem., 1915, 35, 297—305.

THE jack bean (*Canavalia ensiformis*), growing in the West Indies, was found to contain more than fifteen times, and the sword bean (*C. gladiata*) about five times as much urease as the soya bean (*Glycine hispida*); whilst the horse gram (*Dolichos biflorus*) contained about one-fifth, the white lupin (*Lupinus albus*) about one-fiftieth, and the urd bean (*Phaseolus aureus*) about one-three-hundred and fiftieth as much urease as the soya bean. The extract from the jack bean contained much less solid residue than did that from the soya bean, and the urease appeared to be specific for urea; the extract was found to be useful for the removal of urea previous to the determination of amino-acids in urine by the Van Slyke method.—W. P. S.

*A hydrogen-oxidising bacterium from Indian swamp rice soils.* Harrison and Subramania Aiyer. See XVI.

*Influence of various salts on the liquefaction of starch.* Viswanath and others. See XVII.

## PATENTS.

*Potato peelings; Preparation of — for industrial utilisation.* E. Borràs, and Anòn. Borràs, Barcelona, Spain. Eng. Pat. 100,875, Jan. 3, 1916. (Appl. No. 50 of 1916.)

POTATO peelings are boiled with water or steamed, then dried in a stove at a temperature gradually rising from 60° to 130° C. to obtain a product having a certain hardness or rigidity, which may be crushed or ground and subsequently used for the manufacture of glucose, alcohol, etc.—J. F. B.

*Starch and the like; "Depulverisation" of —. Material for use in brewing.* P. Dreesbach, Assignor to Corn Products Refining Co., New York. U.S. Pats. (A) 1,186,893 and (B) 1,186,894, June 13, 1916. Dates of appl. Mar. 30 and Apr. 30, 1915.

A STARCH powder is mixed with a solution of a binder which will form with it a solid mass and is non-injurious for human consumption, e.g., glucose or other sugar, in the proportion of about 1 part of dry binder to 9 of starch; the resulting paste is moulded, dried by heat, and broken up. (2) The material for use in brewing consists of starch substantially ungelatinised, the granules of which are held together in the form of fragments by a binder.—J. F. B.

*Treatment of earthenware filters for the preparation of non-alcoholic beverages from vines and fruit juices.* Ger. Pat. 291,848. See XIXA.

## XIXA.—FOODS.

*Gluten considered from the stand-point of colloid chemistry. Influence of fat and acids on the baking strength [of flour].* K. Mohs. Z. ges. Getreidew., 1915—1916, 7, 218—225, 239—242, 250—260. Z. angew. Chem., 1916, 29, Ref., 274.

IN the preparation of dough the excess of water acts as dispersing medium, the starch and proteins forming the dispersed phase. Gliadin and glutenin have a microscopic honeycomb structure; they are hydrophil colloids and form inelastic gels. When swollen they produce gluten as a result of mutual irreversible coagulation; the glutenin is enclosed by the gliadin, which is present in larger proportion, and hence the gluten tends to resemble gliadin in its properties. If the gliadin content be diminished the formation of gluten decreases rapidly until, ultimately, the gluten can no longer be separated by washing. The extensibility of the gluten depends upon the degree of hydration of the gluten proteins. The destruction of the swollen condition of the inelastic gluten gel in baking is irreversible, that is, the protein-structure of the finished loaf cannot be again swollen. Fats, up to 15%, have a favourable influence on the yield of dough from flour, and on the volume and development of the crumb of the loaf. The effect is due to reversible adsorption of the fat by the gluten proteins. Organic acids produce increased swelling of gliadin and glutenin and increased hydration of the gluten proteins.—A. S.

*Pectin in spices; Determination of —.* T. von Fellenberg. Mitt. Lebensmittelunters. Hyg., 7, 42—61. J. Chem. Soc., 1916, 110, ii., 351—352.

THE method depends on the estimation of the methyl alcohol yielded by the pectin (compare this J., 1915, 574). From 1 to 2 grms. of the sample is placed on a filter and treated with small quantities of boiling 95% alcohol until the filtrate measures about 40 c.c.; after a similar treatment with light petroleum, the contents of the filter are dried, transferred to a flask, and distilled with

40 c.c. of water, 20 c.c. of distillate being collected. The mixture in the flask is now treated, while hot, with 5 c.c. of 10% sodium hydroxide solution, and, after five minutes, 2.5 c.c. of dilute sulphuric acid (1:4) is added, and 16.2 c.c. is distilled over; this distillate is mixed with 5 drops of sodium hydroxide solution and 5 drops of 10% silver nitrate solution and again distilled, 10 c.c. of distillate being collected and once more distilled. The final distillate, measuring exactly 6 c.c., is weighed. Three c.c. of it is then treated with 1 c.c. of an alcohol-sulphuric acid solution (21 c.c. of 95% alcohol and 40 c.c. of concentrated sulphuric acid diluted with water to 200 c.c.) and 1 c.c. of 5% potassium permanganate solution. Comparison solutions containing 5 mgrms., 1 mgrm., and 0.3 mgrm. of methyl alcohol, respectively, are similarly treated at the same time. After two minutes, the mixtures are each treated with 1 c.c. of 8% oxalic acid solution, 1 c.c. of concentrated sulphuric acid, and 5 c.c. of magenta-sulphurous acid solution, and the colorations obtained are compared after the lapse of one hour. The pectin content of the sample is ten times that of the methyl alcohol.

*Cottonseed meal; Nutrition investigations upon —.* A. E. Richardson and H. S. Green. J. Biol. Chem., 1916, 25, 307—318.

COTTONSEED meal contains sufficient protein and fat-soluble growth-promoting substance but the quantity of mineral substances present is inadequate for growth of animals. When mixed with other substances the meal forms an efficient food material. For instance, rats grew and developed normally when fed on a mixture containing cottonseed meal, 45, whole milk powder, 17, starch, 10, and lard, 28%.—W. P. S.

*Palm nut kernel cake; Cause and prevention of rancidity in —.* R. B. Calder. J. Agric. Sci., 1916, 7, 470—472.

AFTER heating for a short time at 70° C., or for a long time at 60° C., palm nut kernel cake can be kept sweet for at least ten weeks. The rancidity is due to a zymogen which, under the influence of warmth and moisture, gives rise to a lipase; the latter is usually destroyed on heating the dry cake, but heating when moist is more certain.—E. H. T.

*Aniline dyestuffs; Anti-coagulating action of acid — on proteins.* A. C. Hollande. Comptes rend., 1916, 162, 959—961.

ON adding an aqueous solution of a basic aniline dyestuff to blood serum, a copious precipitate is obtained, whereas an acid dyestuff produces at most a slight turbidity. If the serum be heated with the acid dyestuff (e.g., Congo Red) no coagulation of protein occurs even at 120° C. By reducing the amount of dyestuff to the point where it is only just sufficient to prevent coagulation on boiling, the serum becomes a transparent jelly when cold. Similar results are obtained with other sera such as white-of-egg, etc. Among acid dyestuffs the following are mentioned in the order of anti-coagulating activity:—Water-soluble Eosin, Orange G, Uranin, Congo Red. The specific character of a protein is modified on boiling the liquid in presence of an acid dyestuff. For example, repeated injection of white-of-egg, which has been boiled with Congo Red for 10 mins., into a rabbit, does not produce precipitins specific for egg albumin in the rabbit serum. Agglutinins, hemolysins and alexins are not destroyed by the addition of acid dyestuffs in the cold. Compounds of acid dyestuffs with proteins are not precipitated by cold 90% alcohol, by nitric acid, or 40% formaldehyde; 10% acetic acid gives a precipitate which is rapidly soluble in excess of the reagent.

Saturation with sodium chloride gives only a slight turbidity, but saturation with ammonium sulphate yields an abundant precipitate. Sera mixed with Congo Red may be sterilised in an autoclave at 120° C. and used as culture media for bacteria. By adding 1 vol. of 2% Congo Red solution to 2 vols. of a serum a mixture is obtained which gelatinises in a few minutes at 100° C. and may be sterilised for 20 minutes at 120° C. without losing its transparency. It is considered that the acid dyestuffs combine with the proteins to form coloured acid-albumins. —C. A. M.

*Urease content of certain beans, with special reference to the jack bean.* Mateer and Marshall, jun. See XVIII.

*Ninhydrin reaction with amino-acids and ammonium salts.* Harding and Warneford. See XX.

*Ninhydrin reaction with amines and amides.* Harding and MacLean. See XX.

#### PATENTS.

*Condensed milk; Manufacture of — and apparatus therefor.* S. S. Cohen, Rotterdam, Holland. Eng. Pat. 7105, May 12, 1915.

AN apparatus for preparing sterilised condensed milk (sweetened or unsweetened) consists of three superposed vessels. The milk is concentrated under reduced pressure in the upper vessel; the connection with the pump is then closed and the milk is allowed to flow into the middle vessel where it is cooled, means being provided for equalising the pressure in these two vessels. When cold, the milk is discharged into the lowest vessel and thence into sterilised receptacles. Filtered compressed air or other gas may be admitted to the top of the lowest vessel to expedite the discharge of the condensed milk. By means of suitable tapped valves provided with filters, air may be admitted to the different vessels after the milk has been concentrated to the desired consistency. —W. P. S.

*Cheese; Process of sterilising — and an improved product produced by such process.* J. L. Kraft, Chicago, Ill. U.S. Pat. 1,136,524, June 8, 1916. Date of appl., Mar. 25, 1916.

CHEESE of the Cheddar type is heated at 175 F° (80° C.) for some time and stirred during this treatment; it is then filled into sterilised receptacles which are hermetically sealed. —W. P. S.

*Earthenware filters for the preparation of non-alcoholic effervescent beverages from wines and fruit juices; Treatment of —.* Gebr. Seyboth Chem. Fabr., Munich. Ger. Pat. 291,848, Aug. 24, 1915.

IN the preparation of aerated beverages from fruit juices and from wine from which the alcohol has been removed by distillation, the liquid is filtered through an earthenware filter which has been impregnated with a fluorine salt capable of combining with the silica of the earthenware and with sodium chloride. By this treatment the microscopic cracks in the filter are partially closed without unduly diminishing the porosity of the filter, and a filtrate quite free from germs is obtained. —A. S.

*Comestibles and their method of manufacture; Powders mainly applicable as —.* S. A. Vasey and U. A. Cleeve, London. Eng. Pat. 9343, June 25, 1915.

THE powder, e.g., oatmeal, pea flour, coffee, is projected by an air-blast into an atomised hydrocarbon, such as petroleum, which is odourless, liquid, and non-volatile at ordinary temperatures. From 1–3% of hydrocarbon is used. —J. H. J.

*Eggs; Art of preserving —.* S. F. Henderson, Assignor to Yester-laid Egg Co., Woodwardville, Md. U.S. Pat. 1,174,008, Feb. 20, 1916. Date of appl., Aug. 28, 1915.

THE eggs are placed in a wire basket and immersed in a bath of "liquid petrolatum." This substance is a mixture of hydrocarbons, chiefly of the methane series, obtained by distilling off the more volatile portions of petroleum and purifying the residue so as to produce a colourless, odourless, tasteless, and non-poisonous oil, which remains liquid on exposure and is non-volatile at ordinary temperatures. After immersion for 15 secs., the eggs are removed and drained. —J. H. J.

*Preparation of potato peelings for industrial utilisation.* Eng. Pat. 100,675. See XVIII.

#### XIXB.—WATER PURIFICATION; SANITATION.

*Waters carrying colloids; "Relative stabilities" in polluted —.* A. Lederer. Chem. News, 1916, 113, 308–309.

IN applying the methylene-blue test for putrescibility to waters carrying colloidal suspensions of clay, sewage matter, etc., the dye is adsorbed by the clay, leaving the liquid colourless and the sediment coloured. This decolorisation of the liquid may be partial or complete, depending upon the amount of colloid present, and prevents any accurate determination of the relative stability of the water. Experiments showed that the methylene-blue adsorbed by the colloid is rendered largely inert as an indicator, the sediment remaining blue long after all available oxygen in the water has been used up. If more than the standard amount of methylene-blue is added and remains in solution, the antiseptic action of the dye affects the result and causes an apparent higher relative stability. Attempts to cause the colloids to settle by means of freshly precipitated coagulants before adding the dye, gave unsatisfactory results. In the presence of colloids, therefore, the methylene-blue test is inapplicable, and resort must be had to the determination of the available oxygen used up by the water. For this the author recommends determining the dissolved oxygen on the spot, bottling other portions of the water with and without the addition of potassium nitrate (this J., 1915, 731) and incubating at 20° C. for 10 days. Then the samples are analysed for dissolved oxygen and nitrites and nitrates. The nitrous and nitric nitrogen is calculated into its equivalent of oxygen, and the total loss of available oxygen during incubation gives the oxygen demand of the water. —J. H. J.

*Water; Field-sterilisation of — by treatment with hypochlorite. Composition and stability of sodium hypochlorite solution.* H. Penau. J. Pharm. Chim., 1916, 13, 377–385.

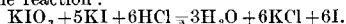
A METHOD proposed for the sterilisation of water for the use of armies in the field consists in adding a large excess of active chlorine and subsequently destroying this excess by the addition of sodium thiosulphate. The sodium hypochlorite solution employed is prepared by dissolving 5 kilos. of Solvay sodium carbonate (75% Na<sub>2</sub>CO<sub>3</sub>) in 40 kilos. of water and adding a mixture of 5 kilos. of calcium hypochlorite and 50 litres of water. After settling, the supernatant liquid is filtered through cloth, and potassium permanganate is added in the proportion of 0.2 gm. per litre of the liquid. The latter contains sodium chloride, 8.7–11.3; sodium hypochlorite, 11.0–11.7; sodium chlorate, 0.7–2.6; sodium carbonate, 3.7–5.8; sodium sulphate, 0.5–2.8; sodium hydroxide, 2.4–2.7 grms. per litre; it yields

about 10.5 grms. of active chlorine per litre, and maintains its strength for at least 2 months. Five hundred litres of the water to be sterilised is mixed with 250 c.c. of this hypochlorite solution and, after 45 mins., the excess of chlorine is destroyed by the addition of 30 c.c. of sodium thiosulphate solution (10 kilos. of the salt per 100 litres of water); the water is ready for drinking after the lapse of a further 5 mins. Wooden tubs or barrels, coated inside with a layer of paraffin wax, are used in the preparation of the hypochlorite solution and in the treatment of the water.

—W. P. S.

*Waters: Control of the purification of — with hypochlorite, after elimination of active chlorine by sodium thiosulphate.* J. Golse. J. Pharm. Chim., 1916, 14, 8—13.

Two methods are described for the detection or determination of traces of thiosulphate in waters. In the first, 20 c.c. of water is treated with 1 c.c. of silver nitrate solution (1 in 20) and just sufficient ammonia to dissolve all silver chloride. The presence of even 1 mgrm. of sodium thiosulphate per litre will be indicated by a faint brown tint due to silver sulphide, and the test can be made quantitative by the use of standard tints. A more sensitive test is based on the action of thiosulphate in reducing iodine liberated by the reaction:



In a separating funnel of 150 c.c. capacity, 100 c.c. of the water, containing 1 c.c. of 5% potassium iodide solution and 1 c.c. of hydrochloric acid (1:10), is treated with sufficient benzene (1 or 2 c.c.) to form a thin layer on the surface. A solution of potassium iodate, containing 0.0144 grm. per litre, is added until, after shaking, the benzene film, viewed at grazing incidence, shows a slight reddish tint. One c.c. of iodate solution corresponds to 1 mgrm. of crystallised sodium thiosulphate per litre of the water. The test is rendered more trustworthy if accompanied by a blank with distilled water. The difference in the volumes of iodate solution required to produce equal tints in the two cases, is a measure of the thiosulphate present.—J. H. L.

*Iodine and bromine in saline waters from petroleum-bearing strata; Determination of —.* D. E. Popa. Bull. Sci. Acad. Roumaine, 1915—16, 4, 308—317. J. Chem. Soc., 1916, 110, ii, 339.

A MODIFICATION of a method proposed by Weszelszky is recommended; the method depends on the oxidation of the iodine to iodic acid by means of chlorine in acid solution, the bromine at the same time being liberated and removed by distillation. A small quantity of bromine is, however, converted into bromic acid, and the modification described consists in a double treatment with chlorine, with intervening reduction, in order to recover all the bromine. 100 c.c. of the water is rendered alkaline with sodium hydroxide, evaporated, the residue is ignited at a low temperature in order to destroy organic substances, then dissolved in water, the solution filtered, and the insoluble portion washed. The filtrate and washings are evaporated to about 70 c.c., transferred to a distillation flask, and acidified with sulphuric acid or hydrochloric acid. 75 c.c. of 1% chlorine water is now added, the flask is connected with a receiver containing 1% potassium hydroxide solution, and the contents of the flask are heated, a current of carbon dioxide being passed through the apparatus when steam begins to enter the receiver. After continuing the distillation for about thirty minutes, the contents of the flask are cooled, 20 c.c. of saturated sulphur dioxide solution (at 0° C.) is added, and the mixture is boiled until practically

all the sulphur dioxide has been expelled; the receiver is meanwhile detached, the alkaline solution transferred to a porcelain dish, and a fresh portion of potassium hydroxide solution introduced. The solution in the flask is then treated with chlorine and the distillation repeated. The united distillates are evaporated, the residue is heated on a boiling water-bath for 45 mins., then dissolved in 130 c.c. of water, the solution treated with potassium iodide and sulphuric acid, and the liberated iodine titrated; its quantity is a measure of the amount of bromine present. The solution remaining in the distillation flask is boiled for about fifteen minutes to remove a small trace of bromine which remains (this amount of bromine is too small to affect the result for bromine, but interferes with the iodine estimation), then cooled, potassium iodide is added, and the liberated iodine titrated.

*Spray-fluids; Fungicidal properties of certain —.* J. V. Eyre and E. S. Salmon. J. Agric. Sci., 1916, 7, 470—507.

THE fungicidal efficiency of a variety of preparations was investigated on 1—2 year old seedlings of the Hop (*Humulus Lupulus* Linn.) bearing the "powdery mildew" (*Sphaerotheca Humuli* (D.C.) Burr.) grown in an unheated greenhouse, and in a few cases on gooseberry bushes infested with American gooseberry-mildew (*Sphaerotheca mors-uvae*) grown in the open. The spraying was done in May, June, and July, by means of a hand "atomiser," and sufficient spray was used to wet thoroughly the infested leaves, untreated leaves being observed on the same plant. None of the following had any fungicidal value: soft soap (1% solution), saponin (0.25%), sodium carbonate (0.3%) and soft soap (1%), sodium thiosulphate (1%) and soft soap (1%). Trials with solutions of sodium hydroxide and soft soap (1%), showed that with concentrations of alkali up to 0.5% the mildew was not killed, although the epidermal cells of the leaves were affected; a 1% solution killed the fungus but "scorched" the leaves badly, and a 1.5% solution killed the leaves after 3 days. A 2% solution of ammonia was practically useless, a 4% solution checked the mildew but seriously affected the leaf-tissue. Preparations of "liver of sulphur" and of ammonium sulphide required the addition of soft soap or similar substance (see also this J. 1916, 378). The fungicidal value of alkaline sulphide solutions is determined neither by the presence of free alkali, nor by the proportion of sulphide-sulphur present, but by the polysulphides present as such, irrespective of the sulphur they deposit on decomposition. Colourless solutions of ammonium hydrosulphide and of ammonium sulphide, containing up to 3.3% of sulphide-sulphur, merely checked the mildew temporarily, and a solution of hydrogen sulphide (0.056% sulphide-sulphur and 1% soap) was useless. A solution containing 0.6% of iron sulphide + 0.5—1.0% of soft soap has a remarkably rapid fungicidal effect; it leaves a rusty-brown deposit, and when made by a method which leaves a trace of yellow ammonium sulphide in it, is quite harmless to foliage and can be applied as a fine spray.

—E. H. T.

*Chemical and physical properties of artificial zeolites.* Von Sigmond. See XVI.

#### PATENTS.

*Water-softening and purifying apparatus.* W. Paterson, London. Eng. Pat. 4275, Mar. 18, 1915. (See Eng. Pat. 10,293 of 1909.)

A TIPPING vessel for the by-passed, measured quantity of water is mounted on a movable shaft, and is provided with levers to operate a double

ended ram, the ends of which are connected by a pipe having controllable outlets, so that as the tipping vessel falls, one of the rams is operated and the water in its cylinder is forced through the connecting pipe; by this means the energy of the falling water within the tipping vessel is absorbed. In connection with this apparatus, there is a tank for the chemical reagent, the contents of which are kept constantly stirred by revolving paddles mounted on the shaft of a water wheel which is actuated by the main flow of water. Numerous cups are mounted on the paddles which are filled with the reagent during rotation and discharge into a hopper connected to a double-compartment, oscillating, measuring vessel. The compartment which is in action is kept full until such time as it is required to be discharged into the water to be treated, the surplus reagent entering the compartment meanwhile, being allowed to overflow back to the reagent tank. In order that the whole contents of the reagent-measuring vessel may be discharged instantaneously, it is connected with the water-measuring vessel by linked levers which operate a loosely-mounted weighted lever. When this is raised to a vertical position, it falls over by its own weight and strikes a pin on the reagent-measuring vessel, thus instantly tipping it. For adding dry reagents to water, a modified apparatus on the same principle is employed.—J. H. J.

*Filter for water.* W. J. Rankin, Tulsa, Okla. U.S. Pat. 1,186,608, June 13, 1916. Date of appl., Dec. 3, 1915.

A CASING is divided by horizontal partitions into an upper, an intermediate, and a lower chamber, all filled with granular filtering material. The water to be filtered is supplied to the upper chamber and passes successively into the other chambers through openings in the partitions, and the flow of water is directed by transverse baffles in the upper chamber and longitudinal guide-plates in the intermediate and lower chambers. Spaced above the floor of the lower chamber is a grating so as to form a drain, and immediately above the drain is an outlet opening in the side of the casing. Guards are provided to prevent the granular filtering material passing into the openings in the partitions and the outlet opening.—A. S.

*Lime-sulphur compounds and solutions; Process for making* —. A. D. Fest, Chicago, Ill. U.S. Pat. 1,186,564, June 13, 1916. Date of appl., Aug. 8, 1914.

SUITABLE proportions of lime and sulphur are mixed with water to a paste and treated with steam in an autoclave. The product is a concentrated solution of 40° B. (sp. gr. 1.38) or over, which is diluted to form an insecticidal spray.—J. H. J.

*Sewage sludge and the like; Treatment of* —. E. A. Paterson, Thorold, Ontario, Canada. Eng. Pats. 3355, Mar. 2, and 10,262, July 14, 1915.

PRESSED sewage sludge is neutralised, if necessary, by the addition of calcium carbonate, then mixed with from 1 to 5% of its weight of sodium silicate, dried at a temperature not exceeding 250° F. (about 120° C.), and submitted to destructive distillation. The treatment with sodium silicate renders the sludge more porous and the hot gases readily penetrate the mass during the distillation.—W. P. S.

*Liquid-treating apparatus.* K. W. Bartlett, Hammond, Ind. U.S. Pat. 1,186,161, June 6, 1916. Date of appl., Mar. 15, 1916.

THE liquid is discharged over a bucket-wheel into a settling tank, the movement of the wheel controlling means for supplying definite quantities of chemical reagent from a separate tank to the settling tank.—W. P. S.

*Electrochemical apparatus [for purifying liquids].* C. P. Landreth, Philadelphia, Pa. U.S. Pat. 1,186,106, June 6, 1916. Date of appl., Oct. 14, 1914. SEE Eng. Pat. 18,564 of 1914; this J., 1915, 978.

## XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.

*Alkaloids; Determination of small quantities of* —. E. Carlinfanti. Boll. Chim. Farm., 1915, 54, 321—323. J. Chem. Soc., 1915, 108, ii., 709—710.

THE estimation of small amounts of morphine or codeine, either in pharmaceutical preparations or for toxicological purposes, may be effected by the following colorimetric methods, a Wolff colorimeter being employed. In the case of morphine, the solution to be examined and a known volume, say 1 c.c., of a 0.5% morphine hydrochloride solution are evaporated separately in basins on a water-bath, and allowed to cool in a desiccator. Each of the residues is dissolved in 5 c.c. of concentrated sulphuric acid, and the liquid introduced into a tube holding about 50 c.c. and fitted with a ground stopper; each dish is washed twice with 3 c.c. of concentrated sulphuric acid, and the washings added to the tube, which is then closed and immersed for fifteen minutes in a boiling water-bath. To the cooled tubes are added 10 c.c. of a mixture of 100 c.c. of concentrated sulphuric acid with two drops of nitric acid (sp. gr. 1.4); on shaking the tubes, the characteristic, blood-red coloration appears. The solutions are then introduced into the cylinders of the colorimeter, in which they are made up to the same height by addition of the small quantities of concentrated sulphuric acid used for washing the tubes.

In the case of codeine, to each of the two aqueous residues, reduced to about 1 c.c. by evaporation on a water-bath at 70°—75° C., 15—20 c.c. of monohydrated sulphuric acid is added cautiously so that the mixture is not heated. The liquid is then introduced into a 50 c.c. flask, together with three quantities of 5 c.c. of the acid used to wash out the dish and 10 c.c. of monohydrated sulphuric acid containing 2 c.c. of 10% ferric chloride solution per 100 c.c. of the acid. After being shaken, the flasks are immersed for fifteen minutes in a water-bath at 80° C., the cooled solutions, which have assumed blue colorations, being introduced into the cylinders of the colorimeter as before.

These methods admit of the estimation of 0.001—0.003 gm. of morphine or codeine hydrochloride to within about 0.0001 gm.

*Alkaloids; Determination of small quantities of* —. E. Carlinfanti and M. Selba. Boll. Chim. Farm., 1916, 55, 225—232. J. Chem. Soc., 1916, 110, ii., 356—357.

UNDER the conditions given for the estimation of morphine (see preceding abstract), acetoxy-morphine (heroin) may be estimated with considerable accuracy; it may be distinguished from morphine, since it colours concentrated sulphuric acid containing nitric acid orange-yellow in the cold and blood-red on heating, and does not reduce iodic acid. Codeine may also be estimated similarly, but for very small quantities of this alkaloid the method previously given (*loc. cit.*) is recommended.

Apomorphine may be estimated as follows: 1—5 c.c. of a 0.1% solution of the hydrochloride is evaporated to dryness in a basin on a water-bath. The residue is allowed to cool in a desiccator, and 10 c.c. of 95% alcohol and 0.1 gm. of sodium bicarbonate immediately added. The whole is then covered with a watch glass and mixed repeatedly during four to five hours, after



which the liquid is poured into a tared flask and made up to volume with the washings of the residue with 95% alcohol. When the suspended sodium bicarbonate has settled, a portion of the clear liquid is decanted into a colorimeter, and the emerald-green coloration which develops compared with that obtained from a known quantity of the alkaloid treated similarly. This method gives good results with quantities of apomorphine of the order 0.001–0.002 gm. For smaller amounts, the authors recommend the following modification of Grimbert and Leclère's method (this J., 1915, 150): To the solution of the alkaloid, made up with water to 3 c.c., are added 5 drops of saturated mercuric chloride solution and then 5 drops of 10% sodium acetate solution. The liquid is boiled for half a minute, cooled, mixed with 1 c.c. of amyl alcohol, and introduced into a 50 or 100 c.c. flask, the vessel being washed out several times with small quantities of 95% ethyl alcohol, and the volume made up with concentrated alcohol. After being shaken, the liquid is left until the mercurous salt settles, the clear solution being compared in the colorimeter with one prepared similarly from a known weight of apomorphine.

In the case of strychnine, a definite volume of the solution containing at least 0.004–0.005 gm. of the alkaloid is heated to boiling with 20–25 c.c. of 15% sulphuric acid solution, recently prepared bromine water being added, drop by drop, until the liquid assumes a pale yellow colour, and the boiling then continued for a few minutes; the presence of strychnine is revealed by a more or less intense reddish-violet coloration. Further addition of a few drops of bromine water turns the hot acid liquid pale yellow, and subsequent boiling renders it reddish-violet again. The cold solution is made up to 50 to 100 c.c., and its depth of colour matched with that of a solution prepared similarly from a known weight of the alkaloid. With a pharmaceutical preparation containing a strychnine salt, a quantity presumably containing at least 0.005 gm. of the base is mixed with an alkali, and the mixture extracted with chloroform, the residue from the latter then being dissolved in 15% sulphuric acid solution and treated as above.

Under the conditions employed in the case of strychnine, brucine gives a salmon-red coloration with bromine water, but, when the alkaloid is present in small proportion, the second addition of bromine water renders the solution colourless. With strychnine, on the other hand, the violet-red coloration persists almost unaltered after a second and even a third treatment with bromine water. In conformity with this behaviour, the proportion of strychnine in *Nux vomica* preparations and other solutions containing strychnine and brucine in approximately equal proportions may be estimated by means of bromine water in the manner described above.

#### *Cocaine and opium; Importation of — prohibited.*

A ROYAL Proclamation, dated July 28th, 1916, prohibits the importation of "all cocaine and all opium" into the United Kingdom, except that imported under the licence of a Secretary of State. The word "cocaine" includes "all preparations, salts, derivatives, or admixtures prepared therefrom or therewith and containing 0.1% or more of the drug." The word "opium" means "raw opium, powdered or granulated opium, or opium prepared for smoking, and includes any solid or semi-solid mixture containing opium." Regulations under Order in Council, dated July 28th, have been framed to carry out the provisions of the above proclamation.

*Picrotoxin.* R. Horrmann. *Annalen*, 1916, 411, 273–314.

THE work of Sielisch (*Annalen*, 1912, 391, 1),

showing that picrotoxin is a compound,  $C_{30}H_{44}O_{13}$ , which readily decomposes into picrotoxinin,  $C_{11}H_{18}O_8$ , and picrotin,  $C_{19}H_{26}O_5$ , is accepted, and these two substances are shown to be dilactones. Hydrolysis with aqueous alkali first gives  $\alpha$ -picrotoxininic acid,  $C_{11}H_{18}O_7$ , and  $\beta$ -picrotinic acid,  $C_{19}H_{26}O_6$ , respectively, and these yield with excess alkali the dicarboxylic acids of picrotoxinin and picrotin,  $C_{11}H_{16}O_8$  and  $C_{19}H_{24}O_6$ , respectively. On account of the readiness with which they are hydrolysed by dilute alkalis and of the stability of the free hydroxy acids, picrotoxinin and picrotin are not considered to be  $\gamma$ -lactones. The powerful reducing properties towards ammoniacal silver and Fehling's solutions characteristic of picrotoxin, etc., are absent in the derivatives with the exception of  $\alpha$ -picrotoxininic acid; hence the production of these acids is not due solely to the splitting of the lactone ring, and further transformation must occur in the alkaline solution. The behaviour of  $\beta$ -picrotoxininic acid,  $\alpha$ -picrotinic acid, and picrotoxinic acid is very different to that of the isomeric  $\alpha$ -picrotoxininic acid and  $\beta$ -picrotinic acid; they are stable to weak oxidising agents and contain a lactone ring which is not attacked even by stronger alkalis  $\alpha$ -Picrotoxininic acid is converted into the  $\beta$ -isomer by boiling with 2*N* sulphuric acid. Of the 6 oxygen atoms in picrotoxinin, 4 are present as lactone and 1 as hydroxyl; in  $\alpha$ -picrotoxininic acid, 2 are present as lactone, 2 as hydroxyl, and 2 as carboxyl; in picrotoxinindicarboxylic acid, 3 are present as hydroxyl, 4 as carboxyl; the corresponding derivatives of picrotin contain one more oxygen atom as hydroxyl. Picrotoxinic acid,  $C_{19}H_{26}O_7$ , and  $\alpha$ -picrotinic acid,  $C_{19}H_{26}O_6$ , are closely related, the latter containing an additional hydroxyl group. There is not yet sufficient evidence to warrant any constitutional formulæ for picrotoxinin and picrotin being advanced.—F. W. A.

#### *Gum in official syrups; Determination of —.* E. Luce. *J. Pharm. Chim.*, 1916, 14, 13–19.

THE author obtained very accurate results by the method of Rocques and Sellier (see this J., 1911, 823), diluting the French official syrup five-fold, and precipitating 25 c.c. of the diluted syrup with 50 c.c. of 95% alcohol and 2 c.c. of saturated alcoholic lead acetate solution. Bellier's method (*Ann. Falsif.*, 1910, 3, 528), though not so accurate, was found sufficiently exact for many purposes. Twenty c.c. of the five-fold diluted syrup is precipitated with 40 c.c. of 95% alcohol and 1 c.c. of a 10% aqueous calcium chloride solution. After 24 hours the precipitate is washed by decantation with 60 c.c. of 65% alcohol in 3 portions, transferred to a tared filter, washed again with 20 c.c. of 65% alcohol, dried for 6 hours in an oven, and weighed. The weight represents dried gum, and is therefore multiplied by 100/88, since the natural moisture-content of gum is about 12%. The ash-content of the dried precipitate is practically the same as that of gum, and may be neglected. These methods, of course, are not applicable to gums containing dextrins.—J. H. L.

#### *Cinnamaldehyde in cinnamon; Colorimetric determination of —.* T. von Fellenberg. *Mitt. Lebensmittelunters. Hyg.*, 1915, 6, 254–266. *J. Chem. Soc.*, 1916, 110, ii, 354–355.

THE value of cinnamon lies in its cinnamaldehyde content rather than in the quantity of total essential oil it contains. A method for the estimation of cinnamaldehyde depends on the coloration which develops when the aldehyde is treated with sulphuric acid and isobutyl alcohol. 1 gm. of the cinnamon is heated just to boiling for ten minutes with 40 c.c. of 95% alcohol in a flask attached to a condenser, and any distillate collected in a 100 c.c. flask. From 30 to 35 c.c. of the

alcohol is then distilled, 100 c.c. of boiled water is added to the residue, and the distillation is continued until the total distillate measures 100 c.c. 5 c.c. of the distillate is then mixed with 2 c.c. of 5% isobutyl alcohol solution (in 95% alcohol) and 3 c.c. of 38% alcohol, 20 c.c. of concentrated sulphuric acid is added, and, after 45 mins., the coloration obtained is compared with that yielded by a known amount of cinnamaldehyde under similar conditions. The standard cinnamaldehyde solution used for comparison contains 2% of the aldehyde in 38% alcohol solution; it may be prepared from the aldehyde-sulphite compound and standardised by a bromine-iodine titration. Nine samples of Ceylon cinnamon were found to contain from 1.31 to 1.84% of cinnamaldehyde; seven samples of cassia-cinnamon contained from 1.23 to 2.77%, and a sample of cinnamon flowers 3.73%.

*Vanillin in vanilla; Colorimetric determination of* — T. von Fellenberg. Mitt. Lebensmittelunters. Hyg., 1915, 6, 267—274. J. Chem. Soc., 1916, 110, ii., 355.

ONE gram of the finely-divided sample is boiled under a reflux apparatus with four successive quantities of about 20 c.c. of water, the extracts are diluted to 100 c.c., 0.5 gm. of kieselguhr is added, and the mixture filtered. Fifty c.c. of the filtrate is extracted five times with alcohol-free ether, using 150 c.c. of the solvent altogether, the ethereal solution is treated with solid calcium chloride, filtered, evaporated to a small volume, and the remainder of the ether removed by a current of air. The residue is warmed to 60° C. with 30 c.c. of water, the solution filtered, and the filtrate diluted to 100 c.c. 5 c.c. of this solution is then treated with 5 c.c. of 1% isobutyl alcohol solution (in 95% alcohol) and 20 c.c. of concentrated sulphuric acid, and the coloration produced is compared, after 45 mins., with that given by a known quantity of vanillin. It is recommended that the vanillin should be estimated separately in the outer and inner portions of the vanilla pod; in the case of normal vanilla, these two portions contain approximately the same quantity of vanillin, and a difference would indicate that some of the vanillin had been extracted from the outer portion.

*Lemongrass oil from Formosa.* K. Kafuku. J. Chem. Ind., Tokyo, 1916, 19, 403—411.

LEMONGRASS oil from Formosa (Hyang-Bow oil) has the following characters: sp. gr., 0.8829 at 22° C., 0.8696 at 40° C.;  $n_D^{20}$  = 1.4850; opt. rot., +0.1° to -0.1°; acid value, 3.1; citral, 64%; total aldehyde, 66.8%. The oil is insoluble in 70%, 80%, and 90% alcohol but is soluble in 1 vol. of absolute alcohol. The terpene fraction after rectification distils at 39°—39.5° C. and consists of myrcene.—T. C.

*Citronella oil from Formosa.* K. Kafuku. J. Chem. Ind., Tokyo, 1916, 19, 411—417.

AN oil distilled in Formosa from a grass supposed to be "Indian geranium" (Formosa citronella oil) possessed the following characters, which are similar in all respects to those of the so-called Java citronella oil distilled from *Cymbopogon Winterianus*, Jowitt (Mahapangiri grass): sp. gr., 0.8868 at 17° C.;  $n_D^{20}$  = 1.4700;  $n_D^{25}$  = 1.4624 in 10 cm. tube; total geraniol, 84.97%; citronellol, 38.98%; geraniol, 37.23% by phthalic anhydride method; soluble in all proportions in 90% alcohol, and in 0.9 vol. of 80% and 4.6 vols. of 70% alcohol.—T. C.

*Japanese oil of pepper. Xanthoxylol.* H. Thoms. Arbeit. Pharm. Inst. Univ. Berlin, 1914, 11, 58—59. J. Chem. Soc., 1916, 110, i., 412.

XANTHOXYLIN (phloracetophenone dimethyl ether)

is present in the oils derived from *Xanthoxylum alatum* and *X. aubertia*, but not in the true Japanese oil of pepper obtained from *X. piperitum*. The yield of the last-named oil was 4.33%, calculated on the weight of the fruits taken (see next abstract).

*Japanese oil of pepper (from Xanthoxylum piperitum, D.C.).* M. Duruttis. Arbeit. Pharm. Inst. Univ. Berlin, 1914, 11, 60—63. J. Chem. Soc., 1916, 110, i., 412. (Compare preceding abstract.)

THE oil had sp. gr. 0.890 at 20° C.,  $n_D$  = 1.47320,  $n_D$  = +26.5. By fractional distillation the liquid was separated into several portions; the most volatile part, b.pt. 175°—178° C., appeared to consist chiefly of dipentene and  $\alpha$ -limonene. In the less volatile portions, palmitic acid and combined acetic acid were present, indications of cuminaldehyde and esterified geraniol also being observed. Methyl cinnamate was not present.

*Croton-resin.* R. Boehm. Arch. Pharm., 1915, 253, 574—585. J. Chem. Soc., 1916, 110, i., 412. (Compare Dunstan and Boole, this J., 1895, 768, 985).

IN order to obtain pure croton-resin from crude croton oil, the latter is treated repeatedly in the cold with methyl alcohol, which dissolves the resin, the fatty acids, and the neutral fatty matter. The acids are removed by treatment with either barium hydroxide or potassium carbonate, which is also employed again after decomposition of the fats by the lipase of powdered *Ricinus* or *Chelidonium* seeds, previously freed from fat. Croton-resin is an almost colourless or pale reddish-yellow, dusty, odourless powder, softening at 80°—90° C., and exhibiting a bitter and, subsequently, an intense and persistent burning flavour. It dissolves sparingly in water and in almost all proportions in organic solvents with the exception of light petroleum, and is highly poisonous, besides exerting a vesicating action. With boiling concentrated hydrochloric acid its alcoholic solution gives a rose-red and then a dark red coloration, a peculiar odour of mould being emitted; with concentrated alcoholic sulphuric acid it gives a grass-green coloration on heating. The iodine value is 76.98, and  $[\alpha]_D$  in chloroform varies for different preparations from +49.96° to 63.23°. Analysis and determination of the molecular weight in naphthalene solution lead to the formula  $C_{21}H_{34}O_6$ . (Compare Paal and Roth, this J., 1909, 611.)

*Evodia ruta carpa; Essential oil of fruit of* — Asahina and Kashiwaki. Apoth.-Zeit., 1916, 31, 115. Z. angew. Chem., 1916, 29, Ref., 282.

A TERPENE, evodene, was isolated from the oil by fractional distillation in the form of a colourless liquid, sp. gr. 0.799, b.pt. 67° C. at 20 mm.,  $n_D$  = 1.4843. A solid crystalline substance, evodiamine, m.pt. 278° C., was also isolated; it yields methyl-anthranilic acid and a base,  $C_{11}H_{19}N$ , when decomposed by heating with alcoholic potassium hydroxide.—A. S.

*Ninhydrin reaction with amino-acids and ammonium salts.* V. J. Harding and F. H. S. Warneford. J. Biol. Chem., 1916, 25, 319—335.

THE ninhydrin (triketohydrindene hydrate) reaction with ammonium salts, first pointed out as a general one by Neuberg (Biochem. Zeits., 1913, 58, 500), takes place only in the presence of hydroxyl ions and these hydrolyse triketohydrindene hydrate to phenylglyoxal- $\alpha$ -carboxylic acid. In the ninhydrin reaction with amino-acids (Ruhemann, Chem. Soc. Trans., 1910, 107, 2030; 1911, 109, 798), it is probable that the amino-acid is decomposed into ammonia and the corresponding glyoxal, the latter acting as the

reducing agent. Whilst the ninhydrin reaction is given by 1% solutions of the ammonium salts of weak acids, the reaction is obtained in the case of ammonium chloride and nitrate only when the solutions of the latter are nearly saturated. The blue coloration produced in the reaction is due to the formation of the ammonium salt of diketohydrindylidene-diketohydrindamine. This colouring matter shows a broad absorption band when examined in dilute solution, the band extending from the red to the green part of the spectrum and blocking out almost the whole of the yellow; the blue colour has a purple appearance when viewed in artificial light, and it is not oxidised by exposure to air.—W. P. S.

*Ninhydrin reaction with amines and amides.*  
V. J. Harding and R. M. MacLean. *J. Biol. Chem.*, 1916, 25, 337—350.

ORGANIC bases of the type  $R_2CH_2NH_2$  and  $R_2CHNH_2$ , where one radicle is negative in character, give the ninhydrin (triketohydrindene hydrate) reaction; other bases which readily yield ammonia or which are readily oxidised also give the reaction. In the case of fatty amines and in the presence of pyridine, the strongest reaction is given by the simplest members. Amides and guanidine and its derivatives do not give the reaction. It is evident that the reaction does not positively indicate the presence of amino-acids (see preceding abstract), and its application to saliva, urine, serum, etc., may lead to erroneous conclusions unless precautions are taken to remove ammonium salts and certain amines.

—W. P. S.

*Uric acid; New salt of — and its application to the analysis [determination] of uric acid and phenol.* J. L. Morris. *J. Biol. Chem.*, 1916, 25, 205—210.

ATTEMPTS to obtain a compound of zinc and uric acid in a pure state were unsuccessful, but there is strong evidence that zinc urate is formed when uric acid and a zinc salt are brought together under certain conditions. Uric acid may be precipitated completely from its solution by means of zinc as follows:—The uric acid solution is acidified with acetic acid, an excess of 10% zinc acetate solution is added, and the mixture is then rendered alkaline to litmus by the addition of saturated sodium carbonate solution. If it is desired to determine the amount of uric acid present, the precipitate formed is collected on a filter, dissolved in acetic acid, the solution treated with a small amount of bismuth carbonate, boiled, and saturated with hydrogen sulphide. The mixed bismuth and zinc sulphides are separated by filtration, the filtrate is boiled to expel hydrogen sulphide, then concentrated to about 10 c.c., and the uric acid estimated colorimetrically by means of phosphotungstic acid. The method is useful for the removal of uric acid from urine previous to the determination of phenol. Four c.c. of the urine is treated with 1 c.c. of 10% zinc acetate solution and a quantity of acetic acid sufficient to dissolve the zinc phosphate formed, the mixture is then rendered just alkaline with saturated sodium carbonate solution, filtered, and the precipitate washed with about 10 c.c. of dilute sodium carbonate solution. The filtrate is boiled with the addition of about 0.5 gm. of calcium carbonate and 1 c.c. of 10% sodium oxalate solution, filtered, the filtrate acidified with oxalic acid, and the phenol determined colorimetrically.—W. P. S.

*Formaldehyde and hexamethylenetetramine; Colorimetric method for the determination of free —.*  
R. J. Collins and P. J. Hanzlik. *J. Biol. Chem.*, 1916, 25, 231—237.

ALiquot portions of the formaldehyde solution

are measured into Nessler tubes, 2 c.c. of phloroglucinol reagent (0.1 gm. of phloroglucinol dissolved in 10 c.c. of 10% sodium hydroxide solution) is added to each, and the mixtures are diluted to 50 c.c. After 3 mins., the colorations obtained are compared with standard colours. The latter are prepared from definite quantities of Congo red solution (0.025% in water containing 5% of alcohol) and methyl orange solution (0.01% in water); 2.5 c.c. of the Congo red solution diluted to 50 c.c. gives the same coloration as 50 c.c. of 0.001% formaldehyde solution when both are viewed in a column 12 cm. in depth. Different samples of Congo red do not always give the same depth of colour and the solution should be standardised against potassium bichromate; 2.5 c.c. of the 0.025% Congo red solution diluted to 50 c.c. should have the same tint as a mixture of 1.7616 gm. of potassium bichromate and 11.5537 grms. of sulphuric acid diluted to 50 c.c. The addition of methyl orange solution to the standards is necessary only when dealing with low concentrations of formaldehyde. The proportions of Congo red and methyl orange corresponding with different concentrations of formaldehyde are given in the following table, the mixtures being diluted to 50 c.c. and viewed in a 12 cm. column:—

Formaldehyde.	Congo red. (0.025% solution).	Methyl orange. (0.01% solution).
%	c.c.	c.c.
0.005	20.0	0
0.0033	11.0	0
0.0025	8.0	0
0.002	5.0	0
0.0016	5.0	0
0.00125	4.0	0
0.001	2.5	0
0.0005	0.85	0.4
0.0040	0.65	0.35
0.0002	0.23	0.18
0.00014	0.20	0.15
0.0001	0.13	0.10

To determine formaldehyde in urine, the phosphates present must be removed by treatment with sodium hydroxide solution and filtration before the above method is applied. Experiments with known quantities of formaldehyde showed that the method was more accurate than several other methods with which it was compared. The colorimetric method may be used to determine hexamethylenetetramine in urine, etc.; the latter is distilled without the addition of acid and the process applied to the distillate. If formaldehyde is also present in the urine, this must be determined previously and its quantity deducted from the total amount.—W. P. S.

*Carbon dioxide from organic compounds; Dynamics of scission of —.* E. Baur and R. Orthner. *Z. physik. Chem.*, 1916, 91, 75—102.

THE authors have studied the decomposition by heat of (i) basic ferric oxalate into ferrous oxalate and carbon dioxide, (ii) salicylic acid into phenol and carbon dioxide, and (iii) sodium salicylate into sodium phenoxide and carbon dioxide. It is shown in the case of basic ferric oxalate that an equilibrium is set up at temperatures between 160° and 200° C.; the equilibrium pressure was measured, and the mass action constant deduced. In the case of salicylic acid the mass-action constant was found to be  $2.7 \times 10^{-4}$  at 203° C.; the dissociation pressure of sodium salicylate at 220° and 230° C. was found to be 143 mm. and 183.5 mm. respectively. In no case could the equilibrium value be obtained from the other side, even when carbon dioxide, at pressures considerably above the dissociation pressure, was employed. The three cases investigated therefore represent

reactions which proceed to an equilibrium that can only be obtained from one side.

*Galactobiose*; *Biochemical synthesis of a* —. E. Bourquelot and A. Aubry. *Comptes rend.*, 1916, 163, 60—62. (See this J., 1915, 159.)

IN experiments similar to those which led to the synthesis of gentiobiose (this J., 1913, 1080), a saturated aqueous solution of galactose treated with emulsin and kept for 5 months at the ordinary temperature yielded a small quantity of a galactobiose, which was not obtained in a crystalline condition.—J. H. L.

*Hydrogen peroxide as a hydrolytic agent.* Dubsky. See III.

*Cetraria islandica* [Iceland moss] as a protective colloid. II. Colloidal gold. III. Colloidal palladium. Gutbier and others. See X.

*Urease content of certain beans, with special reference to the jack bean.* Mateer and Marshall, jun. See XVIII.

#### PATENTS.

*Sera and vaccines*; *Process for producing* —. O. Stiner, Berne, Switzerland. Eng. Pat. 14,972, June 23, 1914. Under Int. Conv., June 21, 1913.

BACTERIA are subjected to the action of ultra-violet rays from a mercury vapour lamp or other source for a sufficient length of time completely to disintegrate them. For example, tubercle bacilli are suspended in a solution of sodium chloride, placed about 10 cm. from the lamp, and exposed to the action of the rays for 20 mins. The endotoxins of the bacteria pass into the suspension fluid, and a serum treated with this fluid has its capacity to destroy bacteria assisted. Tubercle bacilli in tuberculin and diphtheria bacilli in diphtheria toxin, when treated with the rays, yield a portion of their substance to the fluid, and on injecting this fluid into an animal, a serum is produced which acts against the toxin and endotoxin. At the same time, the treatment renders the toxins less poisonous, and suitable for direct injection.—J. H. J.

*Lecithin from vegetable materials*; *Preparation of* — completely free from bitter substances. H. Buer, Cologne. Ger. Pat. 291,494, June 10, 1914.

THE crude lecithin is washed twice by prolonged agitation in a mixing apparatus with acetone containing 10—15% of water and with addition of 0.5—1% of sodium bicarbonate, and then with pure acetone until it again acquires a waxy consistency, after which it is dried *in vacuo* or otherwise at a low temperature. The purified lecithin is quite tasteless and odourless.—A. S.

*Arsenic derivatives of acids and their salts*; *Preparation of* —. F. Heinemann, Berlin. Ger. Pat. 291,614, Feb. 22, 1914. Addition to Ger. Pat. 257,641.

CRYSTALLINE arsenic derivatives of phenylpropionic acid or its derivatives, useful for therapeutic purposes, are prepared by the methods described in earlier patents (see Eng. Pats. 18,732 of 1912 and 10,378 and 10,379 of 1913; this J., 1913, 109; 1914, 218, 438). They are converted into soluble crystalline salts by treatment with alkalis, the halogen being removed.—A. S.

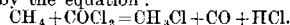
*Hæmoglobin preparation from defibrinated blood from slaughterhouses*; *Production of a solid, stable* —. F. Sgalitzer, Munich. Ger. Pat. 291,911, Mar. 7, 1915.

DEFIBRINATED blood is treated with a neutral salt, e.g., magnesium chloride, which has no action on hæmoglobin, and is then coagulated. The magne-

sium chloride prevents the liquid from solidifying, and the hæmoglobin is obtained in large crystals which can be readily separated by filtration. The crystals can be freed from any adhering magnesium chloride by washing with ice water.—A. S.

*Methyl chloride from methane*; *Manufacture of* —. A. Hochstetter, Vienna. Ger. Pat. 292,089, Nov. 20, 1914. Under Int. Conv., Nov. 20, 1913.

METHYL chloride is prepared by the action of phosgene on methane at a high temperature, for example by leading a mixture of phosgene and methane over a catalyst capable of acting as a chlorine-carrier or of accelerating the reaction by surface condensation. A slight excess of methane is preferably used, and the phosgene may be diluted with inert gases. The reaction is represented by the equation:



—A. S.

*p-Aminophenyl salicylate*; *Preparation of a bromo-derivative of* —. I. Abelin, Berne, Switzerland, and S. Lichtenstein-Rosenblatt, Berlin. Ger. Pat. 291,878, Apr. 21, 1915.

THE  $\alpha$ -bromoisovaleryl derivative of *p*-aminophenyl salicylate,  $\text{HO.C}_6\text{H}_4.\text{CO.O.C}_3\text{H}_7.\text{NH.CO.C}_6\text{H}_4.\text{Br}$ , is obtained by the interaction of an  $\alpha$ -bromoisovaleryl halide and *p*-aminophenyl salicylate or by the bromination of the isovaleryl derivative of *p*-aminophenyl salicylate. It possesses sedative, soporific, and anti-rheumatic properties, produces a gradual lowering of temperature, and acts as an internal disinfectant, and is only slightly toxic.—A. S.

*Thymol*; *Preparation of soluble derivatives of* —. Chem. Fabr. H. Weitz Ges.m.b.H., Berlin. Ger. Pat. 291,935, Apr. 12, 1914.

DOUBLE compounds of thymol and alkali boroformates, soluble in water, are obtained by heating an aqueous solution of an alkali boroformate with an alcoholic solution of thymol.—A. S.

*Hexamethylenetetramine*; *Preparation of derivatives of* —. J. D. Riedel A.-G., Berlin-Britz. Ger. Pat. 292,284, July 27, 1915.

HEXAMETHYLENETETRAMINE combines with perchloric acid to form a non-deliquescent salt,  $(\text{CH}_2)_6\text{N}_4.\text{HClO}_4$ , which is easily soluble in water and has an acid reaction. When treated in aqueous solution with bromine or iodine, this is converted into the dibromo- or di-iodo derivative, respectively. These are stable, insoluble compounds, non-explosive, and possessing a strong antiseptic action.—A. S.

*Organo-metallic compounds*; *Manufacture of* —. W. Schlenk, Jena. Ger. Pat. 292,310, Jan. 13, 1914.

COMPOUNDS containing a C:C, C:N, or N:N linkage are suspended or dissolved in an indifferent medium, and treated with a finely-divided alkali metal, with exclusion of oxygen, moisture, and carbon dioxide. Disodiumdiphenylethane is obtained in this way from stilbene, disodiumdiphenyldianilidoethane from benzylideneaniline, and disodiumhydrazomethane from azomethane. When the products are treated with water, the alkali metal is replaced by hydrogen, whilst treatment with carbon dioxide converts them into alkali compounds of the corresponding carboxylic acids.—A. S.

*2-Phenylquinoline-4-carboxylic acid*; *Preparation of soluble derivatives of* —. Farb. w. v. m. Meister, Lucius, u. Brüning. Ger. Pat. 292,393, July 23, 1914.

SALTS of amino-2-phenylquinoline-4-carboxylic-*o*-

methylsulphurous acid are obtained by condensing amino-2-phenylquinoline-4-carboxylic acid with formaldehyde and a bisulphite. They are easily soluble in water, and possess advantages over other derivatives of 2-phenylquinoline-4-carboxylic acid for therapeutic purposes.—A. S.

**4-Hydroxypyridine; Manufacture of**—B. Emmert, Würzburg. Ger. Pat. 292,456, Dec. 8, 1914.

4-HYDROXYPYRIDINE is obtained by the reduction of 4-hydroxypyridine with an alkali metal and alcohol or with hydrogen gas in presence of a catalyst of the platinum group.—A. S.

**Silver glycocholate and proteins or protein derivatives; Preparation of soluble compounds of**—Farbw. vorm. Meister, Lucius, u. Brünig. Ger. Pat. 292,517, May 26, 1915.

SILVER glycocholate or a compound of the same is treated with a protein or a protein decomposition product, with or without addition of alkali, and the resulting solution is evaporated or treated with a suitable precipitant to isolate the reaction product. The products are soluble in water and serum, and have a neutral, amphoteric, or faintly acid or alkaline reaction. They are of value for therapeutic purposes.—A. S.

**Glycineamide; Preparation of halogen derivatives of**—Act.-Ges. f. Anilinfabr. Ger. Pat. 292,545, May 8, 1914.

COMPOUNDS of the type,  $R_1R_2R_3XN.CH_2.CO.NH_2$ , where  $R_1$ ,  $R_2$ , and  $R_3$  are alkyl groups, and X is a halogen, are obtained by the action of ammonia on alkyl esters of halogentrialkylglycine or of alkyl halides on dialkylglycineamide. They are easily soluble in water and can be used for therapeutic purposes, since they have not the high degree of toxicity characteristic of most organic ammonium compounds.—A. S.

**Quinine and dialkylbarbituric acids; Compounds of**—C. Diehl, Assignor to E. Merck, Darmstadt, Germany. U.S. Pat. 1,185,637, June 6, 1916. Date of appl., Sept. 13, 1912.

SEE Ger. Pat. 249,908 of 1911; this J., 1912, 952.

## XXI.—PHOTOGRAPHIC MATERIALS AND PROCESSES.

### PATENTS.

**Photo-mechanical printing.** C. Blecher, Berlin-Dahlem, Germany. Eng. Pat. 1197, Jan. 25, 1915.

IN the preparation of a diapositive for intaglio printing, the picture area is coloured while the margin is left colourless, so that the carbon print obtained for transfer to the printing cylinder has a margin thicker than any part of the picture. This is a sufficient protection in the etching process and avoids the varnishing of the edges on the cylinder itself.—B. V. S.

**Photographs in colours; Production of**—J. G. Capstaff, Rochester, N.Y., U.S.A. Eng. Pat. 13,429, Sept. 21, 1915. Under Int. Conv., Sept. 21, 1914.

THE usual colour negatives, after developing and washing, are bleached in an acid solution of ferricyanide, bromide, bichromate, and alum, which has a hardening effect on the film roughly proportional to the strength of the image. After thorough washing and drying, the films are dyed in suitable acid dyes, preferably salts of sulphonic acids, in each case complementary in colour to the taking screen. The dye is absorbed by the film in inverse proportion to the amount of hardening.—B. V. S.

**Colour photography.** F. E. Ives, Philadelphia. U.S. Pat. 1,186,000, June 6, 1916. Date of appl., Mar. 13, 1915.

PRINTS are made from the usual colour negatives on

sensitive film which has been coloured with an inert, non-actinic, water-soluble dye. After development the image is bleached in an acid bath of bichromate and bromide, which also hardens the film in proportion to the amount of image. The film may then be dyed with a suitable selective dye, or the soluble parts of the film may first be removed leaving an image in relief which is then dyed, the exposure in this case having been through the film support.—B. V. S.

**Multicoloured screen plates, wholly of glass, for the production of photographs in natural colours.** H. Wieland, Hamm, and E. Mohr, Magdeburg-Sudenburg. Ger. Pat. 291,575, Sept. 11, 1914. Addition to Ger. Pat. 283,551 (this J., 1915, 1168).

THE glass globules of each colour have a different melting point from those of other colours, so that on heating, the globules of one colour melt first and then those of the other colours in succession. An even surface without colourless interspaces or formation of mixed colours at the contiguous edges of globules of different colours, is thus obtained.—A. S.

**Photographic process.** W. F. Fox, Assignor to Kinemacolor Co. of America, New York. U.S. Pat. 1,187,421, June 13, 1916. Date of appl., Dec. 17, 1913.

SEE Eng. Pat. 552 of 1914; this J., 1914, 1227.

## XXII.—EXPLOSIVES; MATCHES.

**Explosives; Fortieth Annual Report of His Majesty's Inspectors of**—for 1915. [Cd. 8272.]

**Factories and magazines.** The total number of factories was 158, of which 33 were under continuing certificate; 23 new factories were licensed during the year. There were 461 magazines, of which 83 were under continuing certificate; 10 new magazines were licensed during the year. Visits were paid to 207 factories and 464 magazines, in addition to factories established by the Ministry of Munitions. **Accidents.** The total number of accidents was 485, viz., in manufacture, 206, in which 21 persons were killed and 170 injured; in keeping, 3, in which 1 person was killed and 4 were injured; in use, and miscellaneous, 276, in which 48 persons were killed and 298 injured. **Importation.** With the exception of 150 lb. imported for the purpose of testing at Rotherham, no blasting explosives or detonators were imported. Fireworks were imported to the extent of 156,500 lb. **Chemical advisers' report.** Of 300 samples examined, 73 were rejected, 26 of these on account of low heat test. The high proportion of rejected samples is considered to be due largely to the greatly increased use of sodium nitrate, which is much less satisfactory than potassium nitrate. **Experiments.** Tests with boxes of percussion primers for 18-pounder quick-firing cartridges showed that these are not liable to explode in bulk. In the case of gaines No. 2, Mark 1, explosion was transmitted from one to another when they were touching, but not when they were packed in trays at a distance of 1½ ins. from centre to centre. An experiment is also described in which 25 lb. of gunpowder was exploded in a conical bronze hopper, ½ in. thick, covered with a wooden board, ½ in. thick. The hopper rested on stout baulks of timber on a platform, 9 in. thick, of concrete reinforced with expanded metal, which was mounted on wooden standards. On firing the powder at the lowest point of the hopper, the concrete platform was completely demolished and the hopper was blown to pieces. So large a quantity of gunpowder should therefore not be allowed on a floor above a loading room in which work-people are employed.—A. S.

## PATENTS.

*Explosives.* A. Aubert and S. Kristensen, Engene, Norway. Eng. Pat. 8129, June 1, 1915. Under Int. Conv., Mar. 1, 1915.

ORGANIC nitro compounds such as trinitrotoluene, picric acid, ammonium picrate, tetranitromethyl-aniline or the like (25 to 85%) are mixed with oxygen carriers (5 to 75%), such as nitrates or perchlorates of ammonium or potassium, which are made in the form of fused hardened globular or angular pieces and distributed evenly throughout the mass, so as to leave broad paths which will allow rapid transmission of detonation. (Reference is directed, in pursuance of Sect. 7, Sub-sect. 4, of the Patents and Designs Act, 1907, to Eng. Pats. 6064 of 1886, 11,400 of 1901, and 20,146 of 1904; this J., 1886, 679; 1901, 932; 1905, 1084).—C. A. M.

*Waste acids from nitrations; Treating—* with a solvent. J. W. Leitch, Huddersfield. Eng. Pat. 15,455, Nov. 2, 1915.

THE waste acid from which nitro-compounds are to be extracted, is run, together with a suitable quantity of solvent, into a mixing tank, which is kept at a suitable temperature, and the mixture then passes into settling tanks. The apparatus comprises a closed vessel in which is a vertical shaft carrying propellers surrounded by cylinders open at each end. The liquid drawn up by these comes in contact with other propellers in the shaft, which drive it downwards and outwards. After thorough admixture the liquid runs continuously through an overflow pipe into the settling tank.—C. A. M.

*Detonator.* W. Runge, Chester, Pa., Assignor to E. I. du Pont de Nemours Powder Co., Wilmington, Del. U.S. Pat. 1,185,830, June 6, 1916. Date of appl., June 30, 1913.

THE casing, which is unobstructed at one end, contains a main charge of explosive which cannot be detonated directly by the flame of a fuse, and a priming charge composed of lead azide, an organic nitro compound (trinitrotoluene), and a binding material (gum arabic).—C. A. M.

*Explosive charges; Method of manufacturing—* by means of liquid air. W. Weber, Hayingen, Germany. Eng. Pat. 8607, June 10, 1915.

SEE U.S. Pat. 1,157,270 of 1915; this J., 1916, 276.

*Explosive; Gelatinised—*. A. Aubert, Saetre, Norway, and S. A. G. Nauckhoff, Liljeholmen, Sweden. U.S. Pat. 1,186,065, June 6, 1916. Date of appl., Jan. 25, 1915.

SEE Eng. Pat. 1283 of 1915; this J., 1915, 1118.

## XXIII.—ANALYSIS.

*Pyrometers; Characteristics of radiation—*. G. K. Burgess and P. D. Foote. Bull. U.S. Bureau of Standards, 1915, 12, 91—178. (See also Waidner and Burgess; this J., 1905, 320.)

THE ordinary types of total radiation pyrometer net with in technical practice (including those of Fery, Foster, Thwing, and Brown) were studied, with special reference to methods of calibration, sources of error, and behaviour under varying conditions of use. The characteristics and proper methods of operating the several types are discussed, together with their application to the measurement of true temperatures. Methods of direct calibration by means of specially designed "black bodies" and of rapid secondary calibration by comparison with a standard pyrometer (sighting on an electrically heated strip of oxidised nickel) are described, and methods of extrapolation are outlined. The thermoelectric pyrometer is considered more accurate than the spiral spring pyrometer, and, with the former,

the potentiometer method of E. M. F. measurement is preferred for work of the highest accuracy, although a galvanometer has been found very satisfactory for most purposes. The principal errors result from imperfections in design and construction, and, in some cases (for example, when there is an appreciable lag in reaching equilibrium), it is important that the instrument be calibrated and used under similar conditions as regards distance from source, aperture of source, and time of exposure. Wide variations in the lag, ranging from a few seconds to an hour or more, were observed among apparently similar instruments. Other errors discussed are those due to stray reflection, convection currents in the pyrometer, atmospheric absorption, size of source, and tarnishing of the receiving mirror; errors of more than 100°C. are readily caused by dirt or oxide upon the surface of the mirror, and errors due to varying the focussing distance may amount to several hundred degrees if proper precautions be not taken. A method of obtaining approximately correct readings when sighting upon a source of insufficient size is described. The Stefan-Boltzmann law,  $E = a(T^4 - T_0^4)$ , is not, as a rule, exactly obeyed by radiation pyrometers, but the equation  $E = aT^4 b$ , in which  $b$  is an empirical constant slightly different from 4, applies with sufficient accuracy for all instruments. The radiation pyrometer generally behaves as a "gray" receiver of energy for the ordinary range of temperatures; that is, the absorption coefficient is less than unity, but independent of the wave-length of the incident radiation. This is no longer true at extremely high temperatures; for example, the effect of selective reflection at the gold mirror of a Fery pyrometer becomes very serious with temperatures such as that of the sun, but it is not practically appreciable below 2500°C.—F. SODX.

*Thorium; Separation of—* from iron with the aid of the ammonium salt of nitrosophenylhydroxylamine ("cupferron"). W. M. Thornton, jun. Chem. News, 1916, 114, 13—14.

THORIUM is precipitated quantitatively from solutions containing no free mineral acid by a slight excess of a 5% "cupferron" solution, and since tartaric acid does not interfere with the precipitation a separation of thorium from iron is possible by this method. The solution of the two metals, containing sufficient tartaric acid to keep the bases in ammoniacal solution, is rendered slightly alkaline with ammonia solution, and colourless ammonium sulphide added in moderate excess. The ferrous sulphide is filtered off, and the excess of hydrogen sulphide boiled off after the addition of 5 c.c. of sulphuric acid to the filtrate. After cooling, 25 grms. of ammonium acetate is added, the volume made up to 400—500 c.c. and an excess of 5% ammonium nitrosophenylhydroxylamine solution added. The precipitate is filtered off, washed with 1% ammonium acetate, transferred to a tared platinum crucible, ignited to thorium dioxide, and weighed.—G. F. M.

*Cadmium; New method for the determination of—*. S. Kragen. Akad. Wiss. Wien, Mar. 30, 1916. Chem.-Zeit., 1916, 40, 530.

THE precipitate produced by the addition of pyridine to a solution of cadmium chloride has the composition of a double compound of 1 mol. of cadmium chloride with 2 mols. of pyridine; on heating in an air-bath at 120°C. half of the pyridine is expelled. The precipitate may be used for the gravimetric determination of cadmium. Alternatively, in the double salt containing 2 mols. of pyridine, the latter may be determined by alkalimetric titration, using Patent Blue as an indicator. The pyridine compound affords a means of separating cadmium from copper, but a

satisfactory quantitative separation has not yet been devised.—J. F. B.

*Washing precipitates for peptisation.* [Preparation of colloidal solutions.] H. N. Holmes and R. E. Rindfusz. J. Phys. Chem., 1916, 20, 522–527.

COMPARATIVE experiments with precipitated ferric arsenate indicated that to remove the adsorbed ions from a flocculent precipitate, the best method is to shake the precipitate with as much hot water as the filter paper will hold, preferably with addition of some clean sand. The mixture, with the exception of the sand, is thrown on to the filter to drain, the precipitate again transferred to the shaking bottle and the treatment with hot water, etc., repeated as many times as may be necessary.—A. S.

*Data on the oxidation of automobile cylinder oils.* Waters. See IIA.

*Decomposition of tetrathionates in alkaline solution as a source of error in certain iodine titrations.* Chapin. See VII.

*Determination of total carbon in iron and iron alloys.* Heinrich and Roger. See X.

*New method of determining the gases in iron.* Goerens and Paquet. See X.

*The ammonia test for sulphite lyes.* Oman. See V.

*Recovery of ammonium molybdate from filtrates in the determination of phosphorus in steel and iron.* Friedrich. See X.

*Distribution of silver between metallic lead and litharge-containing slags.* Dudley. See X.

*Chemical assay of tin ores.* Matheson. See X.

*Determination of phosphoric acid by the citro-uranium method.* Crispo and Tuinzing. See XVI.

*Determination of sucrose in cane products by direct polarisation after destruction of the reducing sugars.* Muller. See XVII.

*Determination of lead [in sugar solutions] as sulphite.* Pellet. See XVII.

*Rapid determination of the sulphate content of wine.* Pritzker. See XVIII.

*Determination of essential oils [essences] in liqueurs.* Rocques. See XVIII.

*Urease content of certain beans, with special reference to the jack bean.* Mateer and Marshall, jun. See XVIII.

*Determination of pectin in spices.* Von Fellenberg. See XIXA.

*Determination of "relative stabilities" in polluted waters carrying colloids.* Lederer. See XIXB.

*Control of the purification of waters with hypochlorite after elimination of active chlorine by sodium thiosulphate.* Golse. See XIXB.

*Determination of iodine and bromine in saline waters from petroleum-bearing strata.* Popa. See XIXB.

*Determination of small quantities of alkaloids.* (1) Carlinfanti. (2) Carlinfanti and Scelba. See XX.

*Determination of gum in officinal syrups.* Luce. See XX.

*Colorimetric determination of cinnamaldehyde in cinnamon.* Von Fellenberg. See XX.

*Colorimetric determination of vanillin in vanilla.* Von Fellenberg. See XX.

*Ninhydrin reaction with amino-acids and ammonium salts.* Harding and Warneford. See XX.

*Ninhydrin reaction with amines and amides.* Harding and MacLean. See XX.

*New salt of uric acid and its application to the determination of uric acid and phenol.* Morris. See XX.

*Colorimetric determination of free formaldehyde and hexamethylenetetramine.* Collins and Hatzlik. See XX.

## PATENTS.

*Gas-analysing apparatus.* H. L. Lowe, Pittsburgh, Pa. U.S. Pat. 1,188,014, June 6, 1916. Date of appl., Feb. 27, 1911.

THE gas is passed from a container through an absorbent (to remove a desired constituent) and is then conducted into a second container; means are provided for measuring the ratio of the difference of the pressure of the gas before and after such treatment to its original pressure.—W. P. S.

*Granular material; Process and apparatus for separating and analysing.* J. C. Pearson, Chevy Chase, Md. U.S. Pat. 1,186,525, June 6, 1916. Date of appl., Apr. 26, 1916.

A DEFINITE quantity of the material is maintained in a continual state of movement by means of a downwardly directed current of gas; the mixture of gas and fine particles is then passed up a vertical tube at a uniform rate of flow and the suspended particles are removed at the upper end of the tube. The treatment is continued until the material is free from particles below a predetermined size, and the proportion of material thus separated is determined.—W. P. S.

## Trade Report.

*Prohibited exports. Amendments in and Additions to List.* Order in Council, July 26, 1916.

THE following headings have been deleted from the list of prohibited exports (see this J., 1916, 620):—(1) Anthracene oil; (1) Coal tar, all products (except creosote) obtainable from and derivatives thereof, suitable for use in the manufacture of dyes and explosives, whether obtained from coal tar or other sources, and mixtures containing such products or derivatives; (3) Creosote; (1) Green oil, (1) Sulphuric acid; (3) Oils, creosote, except wood tar oil; (3) Pitch, coal tar; (3) Pitch, rosin; (3) Pitch, wood; (2) Pitches derived from fats, greases, oils or fatty acids; (2) Rum and imitation rum; (3) Syrups which may be used as food for man, and molasses produced from cane sugar.

The following headings are added:—(1) Cast iron pipes; (3) Anthracene oil and mixtures and preparations containing anthracene oil; (1) Coal tar, all products obtainable from and derivatives thereof, suitable for use in the manufacture of dyes and explosives, whether obtained from coal tar or other sources, and mixtures and preparations containing such products or derivatives (except anthracene oil and green oil and mixtures and preparations containing these oils); (3) Creosote and creosote oils (except wood tar oil) and mixtures and preparations containing such creosote or creosote oils; (3) Green oil and mixtures and preparations containing green oil; (1) Sulphuric acid and mixtures containing sulphuric acid; (1) Molasses; (3) Pitches and all mixtures, preparations and commodities of which pitch forms an ingredient; (3) Potable spirits of a strength of less than 43° above proof; (3) Quercitron bark extract; (3) Syrups which may be used as food for man.

### Restrictions on importation.

THE following interpretations, rulings, and decisions respecting prohibitions of importation have been arrived at by the Department of Import Restrictions:—

*Prohibited:* Basalt lava stones, cement, enamel ware, fireclay goods, granulated crystal quartz, oleine, sandstone, stearine.

*Not prohibited:* Acetic anhydride, antimony ware, barytes, casein, caustic potash, china stone, glassware, graphite, magnesia mantle rings, pulverised metal (for hardening concrete floors), oxalic acid, steatite, talcum powder.

A general licence has been given to H.M. Customs Authorities for the importation of glacial acetic acid and magnesite.

